

MINING AND MANUFACTURE
OF
FERTILIZING MATERIALS
AND
THEIR RELATION TO SOILS

BY
STRAUSS L. LLOYD, E.M.

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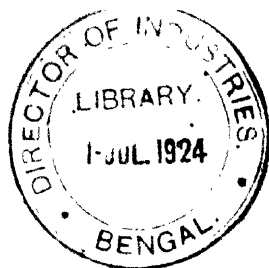
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PREFACE

It is to be hoped that the present volume has unique merits of its own, and will appeal not only to manure manufacturers but to farmers, as well as to agricultural students and all those who take an intelligent interest in the subject of agricultural chemistry. Common sense dictates that it is equally important for the student of agriculture to be able, if need be, to effect the synthesis of a manure as to be able to carry out the analysis thereof. The student who can construct, mentally, a formula for a manure to yield, whether by dry mixing or wet mixing, certain predetermined results on analysis, is more highly trained than he who can use the faculties of destruction to resolve a manure into its constituent elements by following a treatise on agricultural chemical analysis, and that too often by methods which he would have to unlearn if he entered a fertilizer factory, where he would have to analyze manures and raw materials against chemists of some reputation.

STRAUSS L. LLOYD.

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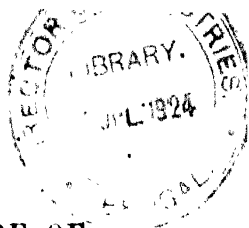
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MINING AND MANUFACTURE OF FERTILIZING MATERIALS

CHAPTER I

CHEMISTRY OF FERTILIZERS

The Four Fundamental Laws - Nitrogen - Potash - Phosphoric Acid - Lime - Terms Used in Analyses - Loss of Fertilizer in Soils - Indirect Fertilizers - Direct Fertilizers.

THE systematic scientific study of agriculture was commenced about sixty years ago, and it is to the celebrated German agricultural chemist Justus von Liebig that we owe the following four elementary laws, which are the foundation of the best modern practice.

I. A soil can be termed fertile only when it contains all the materials necessary for the nutrition of plants, in the required quantity, in the proper form.

II. With every crop, a portion of these ingredients is removed. A part of this is again added from the inexhaustible store of the atmosphere; another part, however, is lost forever if not replaced by man.

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III. The fertility of the soil remains unchanged if all the ingredients of the crops are given back to the soil. Such a restitution is effected by manure or fertilizers.

IV. The manure produced in the course of farming is not sufficient to maintain permanently the fertility of a farm; it lacks the constituents which are annually sold in the shape of grain, hay, milk, and live stock.

These laws cover the whole subject, but to understand them so that they may be applied at work in the field, it is necessary to have a fair idea of the sources of plant food of the different kinds, and how best to use these different kinds for different crops.

It is generally understood that all manures or fertilizers are valuable for the nitrogen, potash, and phosphoric acid they contain. Though other substances are needed for plant growth, they are almost always present in the soil in sufficient quantity. Lime might be made an exception, although its use is largely to improve the mechanical condition of the soil, and cure it of sourness. Lime also aids in rotting the vegetable matter.

The influence of nitrogen in its various forms upon plant growth is shown by at least three striking effects. The growth of stem and leaves is greatly promoted, while that of buds and flowers is retarded. Ordinarily, most plants, at a certain period of growth, cease to produce

new branches and foliage, or to increase those already formed, and commence to produce flowers and fruits, whereby the species may be perpetuated. If a plant is provided with as much available nitrogen as it can use just at the time it begins to flower, the formation of flowers may be checked, while the activity of growth is transferred back to and renewed in stems and leaves, which take on a new vigor and multiply with luxuriance. Should flowers be produced under these circumstances, they are often sterile and produce no seed.

The next effect of nitrogen upon plants is to deepen the color of the foliage, which is a sign of increased vegetative activity and health. Another effect of nitrogen is to increase in a very marked degree the relative proportion of nitrogen in the plant.

Potash is essential to the formation and transference of starch in plants. Starch is known to be first formed in the leaves of plants, after which in some unknown way it becomes soluble enough within the plant cells to enable it to pass through the cell-walls gradually and later to be carried into the fruit, where it accumulates and changes back to its insoluble form. It is well established that potash is intimately connected with the formation of starch in the leaves and with its transference to the fruit. No other element can take the place of potash in performing this work. Potash is important on account

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of its influence upon the development of the woody parts of stems and fleshy portions of fruits.

Experiments have shown that plants will die before reaching maturity unless they have phosphoric acid to feed upon. Phosphates appear to perform three distinct functions of plant life.

They aid in the nutrition of the plant by furnishing the needed quantities of phosphoric acid.

They aid the plant, in some way not well understood, to make use of or assimilate other ingredients. Phosphates are found in the seeds of plants, and, as already stated, a plant does not come to maturity and so does not produce seeds, unless phosphates are present in the soil for the plants to feed upon. The liberal application of available phosphate compounds appears to hasten the maturity of plants.

Certain forms of phosphates render the albuminoids sufficiently soluble to enable them to be carried from the growing parts of plants to the seeds, in which they accumulate in quantity.

The chief function of lime is to improve the mechanical condition of the soil by loosening heavy clay soils and also by holding together and giving body to light sandy soils. Lime aids in the decomposition of animal and vegetable matter, such as vegetable mould, stable-manure, etc., and tends to convert them into available plant food.

In using lime, care should be taken not to

use too large quantities at a time; and, ordinarily, it is best to use it in connection with a liberal application of nutritive fertilizers. Lime can be used with much advantage on freshly drained swamp-lands and also on lands newly cleared.

Fertilizer dealers and manufacturers treat the different forms of fertilizers and fertilizer materials separately, and it is important that one should be familiar with these trade names, and understand what they mean.

The following list contains most of the terms used in stating fertilizer analyses.

Nitrogen is expressed as: (A) Nitrogen, (B) Ammonia, (C) Nitrogen equal (or equivalent) to Ammonia.

Phosphoric Acid is expressed as: (A) Phosphoric Acid, (B) Soluble Phosphoric Acid, (C) Reverted Phosphoric Acid, (D) Precipitated Phosphoric Acid, (E) Available Phosphoric Acid, (F) Soluble and Available Phosphoric Acid, (G) Insoluble Phosphoric Acid, (H) Total Phosphoric Acid, (I) Phosphoric Acid equal (or equivalent) to Bone Phosphate of Lime.

Potash is expressed as: (A) Potash, (B) Potash (actual), (C) Potash S. (or Sul.), (D) Potash (Soluble), (E) Potash as Sulphate, (F) Potash equal (or equivalent) to Sulphate of Potash, (G) Sulphate of Potash, (H) Potassium Oxide.

(A) Nitrogen is a gas, and, in this form, can-

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not be used in fertilizers. Therefore, whenever we speak of nitrogen in fertilizers, we do not mean that nitrogen exists in them as simple nitrogen. The nitrogen in fertilizers is always combined with other elements, and may be present in one or more different forms: (1) in the form of nitrates, as nitrate of soda; (2) in the form of ammonia compounds, as sulphate of ammonia; and (3) in the form of organic matter, animal, or vegetable, as dried blood, meat, tobacco-stems, etc. Chemical analysis, according to official methods, does not attempt to ascertain and state in which form or forms the nitrogen is present in a fertilizer.

When, therefore, nitrogen is expressed in an analysis or guarantee as "nitrogen," it refers to the entire amount of nitrogen present without regard to the particular form or forms in which it is present.

(B) Ammonia consists of nitrogen combined with hydrogen. A pound of nitrogen will form more than a pound of ammonia, because the ammonia formed from a pound of nitrogen will contain that pound of nitrogen plus the necessary amount of hydrogen added to form ammonia. The chemical relations of nitrogen and ammonia are such that 14 pounds of nitrogen will unite with exactly three pounds of hydrogen, and will, therefore, produce just 17 pounds of ammonia; or 1 pound of nitrogen will make 1.214 pounds of ammonia.

(C) Nitrogen equal or equivalent to ammonia is a form of expression which simply means that the nitrogen is stated not as nitrogen but as ammonia,

It would be better on every account if all guarantees stated simply nitrogen and never mentioned ammonia at all. As a matter of fact, compounds of ammonia are quite uncommon in commercial fertilizers, because nitrogen in this form is the most expensive and, therefore, least used. Strictly speaking, the term ammonia should never be used except when sulphate of ammonia or some similar compound is present in the fertilizer.

(A) Phosphoric Acid, as used in connection with fertilizers, is a compound containing phosphorous and oxygen, which in fertilizers is found never by itself, but in combination with lime. Phosphoric acid stands for a certain amount of phosphate of lime. We may say roughly that one part of phosphoric acid is equivalent to about two parts of phosphate of lime, but it is exactly 2.1831 and the percentage of phosphoric acid multiplied by this number will give the percentage of "bone phosphate of lime." But we know that phosphoric acid exists in several different forms.

(B) Soluble phosphoric acid represents the amount of phosphate of lime that dissolves easily in water; it is formed by treating with sulphuric acid some form of insoluble lime phosphate. The phosphate thus formed is readily soluble in

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(C) Reverted phosphoric acid is formed from soluble phosphoric acid under conditions to be explained hereafter.

(D) Precipitated phosphoric acid is simply another name for reverted phosphoric acid.

(E) Available phosphoric acid includes both the soluble and reverted form of phosphoric acid, because both forms are available for the use of plants.

(F) Soluble and available phosphoric acid is an expression which means the same as available.

(G) Insoluble phosphoric acid represents the form of phosphoric acid in raw phosphate of lime, and which is of least value for agricultural purposes.

(H) Total phosphoric acid represents the entire phosphoric acid compounds without regard to the forms in which they exist. The total phosphoric acid is, therefore, the sum of the soluble, reverted and insoluble forms; or, to state it in another way, the sum of the available and insoluble forms.

(I) Phosphoric acid equal (or equivalent) to bone phosphate of lime is an expression which usually means nothing more nor less than insoluble phosphoric acid.

(A) Potash, as used in connection with fertilizers, always means a compound containing potassium and oxygen, known chemically as potassium oxide. Potash is never found as such

in fertilizers, but chemists use this form of expressing the results of analyses as a convenient standard for reference. Fertilizers generally contain potash in such forms as sulphate of potash, muriate of potash, or carbonate of potash. Instead of stating the amount of sulphate, muriate, or carbonate of potash in a fertilizer, its equivalent amount is stated only in the form of actual potash in giving the results of analyses.

(B) Potash actual is simply another name for potash, as distinct from sulphate, muriate, etc.

(C) Potash S. (or Sul.) means sulphate of potash. This is quite often used by manufacturers in giving guarantees.

(D) Potash soluble represents the amount of potash that dissolves in water and is available for the use of plants. The different forms of potash commonly used in fertilizers are readily soluble in water, otherwise they would not be available for the use of plant life.

(E) Potash as sulphate means simply sulphate of potash.

(F) Potash equal (or equivalent to sulphate of potash) is an expression which means simply sulphate of potash.

(G) Sulphate of potash signifies that this compound is actually present in the fertilizer, and that there is no muriate of potash present.

(H) Potassium oxide means the same as potash, or actual potash.

The phosphoric acid in raw materials such as

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ground bone or ground phosphate does not readily leach out of the soil. In specially prepared materials, however, like dissolved bone or dissolved phosphate (acid phosphate) the phosphoric acid is quite soluble and would be removed from the soil by drainage water, were it not for the fact that immediately after application the phosphoric acid becomes changed into another form, which is not apt to leach away.

The mineral forms of nitrogen, such as nitrate of soda and sulphate of ammonia, both dissolve easily in water, hence they would soon wash into the subsoil and out of reach of the plants. The so-called organic forms of nitrogen, like cotton-seed-meal, tankage, fish-scrap, dried blood, etc., are less soluble, and experience indicates that they are largely retained in the soil. It is a matter of observation also that there is little loss of nitrogen by drainage when the soil is covered with vegetation, because the roots of the growing plants absorb nitrogen very readily.

Potash, it has been found by experience, does not wash away to any appreciable extent, because it forms certain combinations in the soil which are not so soluble, but which at the same time are readily available to the growing crops.

In addition it may be said, in general, that loss of plant food is greatest in sandy soils; the coarser the sand, the greater the loss, the other conditions being the same. Clay and humus have very marked power in retaining plant food.

A stimulant or indirect fertilizer is one which does not in itself furnish directly to the soil any needed plant food, but whose chief value depends upon the power it possesses of changing unavailable into available forms of plant food. The stimulant or indirect fertilizers which have been most commonly employed are lime, gypsum, and common salt or sodium chloride.

Gypsum, or land-plaster, known chemically as calcium sulphate, or sulphate of lime, in some manner aids the process of nitrification, by which ammonia and the nitrogen of organic matter are converted into nitric acid and nitrates. It also acts upon the insoluble forms of potash and other elements of plant food, converting them into soluble and available forms; it is of value on certain soils to certain crops, such as clover, peas, lucerne and similar plants.

Quick or burnt lime, or calcium oxide, commonly called lime, produces changes in both the physical and the chemical character of soils. Freshly burned lime acts chemically upon soils by decomposing vegetable and mineral matter present in the soil and changing them into forms which are available as food for plants. Thus lime acts upon insoluble mineral substances containing potash, etc., and converts them into soluble forms. Lime aids in the decomposition of animal and vegetable matter, such as vegetable mould, stable-manure, etc., and tends to convert them into available plant food. In using

lime, care should be taken not to use too large quantities at a time, and, ordinarily, it is best to use it in connection with a liberal application of nutritive fertilizer. Lime can be used to advantage on freshly drained swamp-lands and also on lands newly cleared.

The explanation of the chemical action of lime on soils may be in order here. Before nitrogen in ammonium sulphate or organic substances can be taken up by plant life, it must be converted into nitrates. The nitrogen in organic substances is chiefly in an albuminoid form. The first decomposition which such substances undergo results in the production of ammonia. The oxidation necessary for the conversion of ammonia into nitric acid is dependent upon the presence of a so-called "nitrifying" organism, which is a bacillus to which the name of "nitromonas" has been assigned. The organism requires the usual mineral constituents, e.g., phosphates, for its growth, and free access of air, on which account it is not active in the ground at a greater depth than six feet. The formation of nitrates appears to be always due to the action of the same organism; nitrites, on the other hand, are produced by several different species, which vary with the locality. In order that all the ammonia may be converted into nitric acid, a fixed base must be present, like lime, otherwise ammonia nitrate is the final product. The temperatures between which the organisms can act are 3 and

55 degrees C., 37 degrees C., being that at which they are most active. Darkness is favorable to their development. The process of nitrification is but one phase of the general oxidizing action which is associated with the growth of these bacilli. Thus they are capable of converting iodides into iodates. "Denitrifying" organisms appear also to exist in the soil, capable of reducing nitrate even to free nitrogen. These become active when the soil is water-logged, and are inimical to plant life.

The process of nitrification is so rapid that ammonium sulphate is scarcely less readily assimilated than is sodium nitrate. There is, however, a certain amount of difference in the quantity of certain crops when manured with nitrate and ammonium sulphate respectively, which will be found as set forth. Another difference in their action is on the soil itself; before the nitrification of ammonium sulphate can be completed, the sulphuric acid must be removed by a base—e.g., lime—in the soil, and a further quantity of base will be required by the nitric acid when formed.

Common salt has an indirect fertilizing value which is mainly due to the fact that it has the power of changing unavailable forms of plant food, especially potash, into available forms.

It should be kept in mind that these stimulant fertilizers, that is, gypsum (or plaster), lime, and salt—are not used for the plant food contained in them; hence, as used, they do not furnish

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needed plant food. The chief value of their use lies in the fact that they can change unavailable into available forms of plant food. It can readily be seen that, when stimulant fertilizers are used exclusively for a term of years, the soil each year loses nitrogen and phosphoric acid, which are not replaced. The inevitable result of such treatment is the exhaustion of these important food constituents from the soil. This affords an explanation of the question often raised now as to why the application of land-plaster does not give such results in crop yields at present as in former days. When land-plaster was the only fertilizing material added to soils for years in succession, it was possible to produce increased crops so long as there were in the soil enough compounds of nitrogen, potassium and phosphorus to be rendered available by the action of the land-plaster. When, therefore, these forms of plant food were largely removed, there was nothing for the land-plaster to act upon in order to increase the supply of available food material. The land-plaster furnished no needed food, but simply helped the crop to use more rapidly the store of plant food present in the soil.

Direct fertilizers contain forms of plant food, which contribute directly to the growth and substance of plants. Such materials, as have already been mentioned, contain nitrogen, potash, and phosphoric acid compounds, or any two, or all three of these materials.

CHAPTER II

ORIGIN AND COMPOSITION OF SOILS

Origin of Soil—Geologically Considered—Chemical Elements
• Present — Non-metals — Metals

THE term soil, in its broadest sense, is used to designate that portion of the surface of the earth which has resulted from the disintegration of rocks and the decay of plants and animals, and which is suited, under proper conditions of moisture and temperature, to the growth of plants. It consists, therefore, chiefly of mineral substances, together with some products of organic life, and of certain living organisms whose activity may influence vegetable growth either favorably or otherwise. The soil also holds varying quantities of gaseous matter and of water, which are important factors in its functions. The soil cannot be regarded as entirely dead matter, but as containing living organisms exhibiting many most remarkable biological phenomena.

Agriculturally considered, the soil proper is the older and more thoroughly disintegrated superficial layer of the earth, which has been longest exposed to weathering and the influences of organic life. It varies from a few inches to several

feet in depth. The term subsoil is usually applied to a layer of soil beginning at the usual depth of cultivation and of a thickness of from 6 to 9 in. The surface of demarcation of change of color is sometimes regarded as the upper superficial boundary of the subsoil. The term soil and subsoil are therefore not always used with the same relative signification. The subsoil is not, as a rule, so thoroughly disintegrated as the soil, since it is protected in a measure by the overlying material. It usually contains less organic matter than the soil. There is freer circulation of air in the soil than in the subsoil, and the metallic elements usually exists in the upper layers as higher oxides. There is usually a notable difference in color between the soil and subsoil, and frequently a very sharp color line separates the two.

Geologically considered, the soil is that portion of the earth's crust which has been more or less thoroughly disintegrated by weathering and other forces from the original rock formations, or from the sedimentary rocks, or from the unconsolidated sedimentary material. The soil has, therefore, the same essential constitution as the general mass of the earth, except that this débris has been subjected to the solvent action of water and the influence of organic life.

The chemical elements present in the soil are naturally some or all of those which were present in the original rocks. For purposes relating to agriculture, it is not necessary to take into

account the rare elements which may occur in the soil, but only those need be considered which are present in some quantity and which enter as an important factor into plant growth or modify in some manner its physical properties. Of the whole number of chemical elements less than one-third are of any importance in soil investigations. These elements may be grouped into two classes, the non-metals and the metals as follows:

<i>Non-metals.</i>	<i>Metals.</i>
Oxygen	Aluminum
Silicon	Calcium
Carbon	Magnesium
Sulphur	Potassium
Hydrogen	Sodium
Chlorine	Iron
Phosphorus	Manganese
Nitrogen	Barium
Fluorine	Titanium
Boron	Chromium

Oxygen exists in the free gaseous state in the atmosphere of which it constitutes about one-fifth by bulk, and in combination with other elements it forms nearly half the weight of the solid earth, and eight-ninths by weight of water. It enters into combination with most of the other elements, forming what are known as oxides, and with many of the elements it unites in several proportions, forming oxides of different composition. Com-

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bined with silicon, carbon, sulphur, and phosphorus, it forms an essential part of the silicates, carbonates, sulphates, and phosphates, most of which are very abundant and all of which are very widely distributed in the earth's crust. In this form it is exceedingly stable and is rarely set free. With the exception of the oxides of silicon and iron these oxides seldom occur uncombined with the metals as constituents of rocks or soils. The oxides of iron very commonly occur as such in rocks and soils, and play a very important part in organic life. The several oxides of iron very frequently determine the color of soils; as the iron is more or less oxidized, or as it is exposed more or less to access of air, the color of the soil changes. These oxides of iron also play an important part in the absorptive capacities of soils for moisture and other physical conditions of soils, and also in the oxidation of organic matters in the soils. Many organic substances, and even the roots of growing plants when deprived of free access of air, can readily secure oxygen from the iron oxide, thus reducing the iron to a lower form of oxidation, the oxygen being used for the oxidation of the organic matter or for the needs of the growing plant; while the lower oxide of iron can easily take up the oxygen of the air and again be converted into a higher oxide ready again to give up a part of its oxygen and thus serve as a carrier.

Silicon never occurs in the free state, but com-

bined with oxygen it forms silica, which constitutes free or in combination, more than one-half of the earth's crust. The oxide of silicon occurs in the very common form of quartz, and as silicate of alumina, lime or magnesia silicon forms an essential part of many minerals, such as the feldspars, amphiboles, pyroxenes and the micas, besides being an essential ingredient of many other minerals. Silica is relatively very slightly affected by the ordinary forces concerned in the decay of rocks, and even after the crystals of feldspars, micas and other common minerals occurring in rocks have been disintegrated it remains as hard grains of sand, forming the bulk of most soils. By far the largest part of silicon in soils is in the form of grains of quartz more or less modified. This form of silica is probably chemically inert in regard to plant growth but it plays a very important part in the physical structure of soils in its relations to plant nutrition.

Carbon as an elementary substance occurs as diamond and graphite and in an impure form as anthracite and bituminous coals. In peat and mucks carbon is the chief constituent. This substance is also contained in the organic matters of the soil known as humus, and the relation of the carbon to nitrogen often throws important light upon the amount and character of the nitrogenous matters. The humus content of the soil also affects its relation to water and to the absorption,

retention and radiation of heat. In combination with oxygen it forms the chief food of growing plants, the carbon of the carbon dioxide of the air being elaborated into the tissue of the plants and the oxygen returned to the atmosphere. The content of carbon dioxide in the air is from three to five parts per 10,000 by volume. As a constituent of carbonates this element helps to form some of the most important ingredients of the earth's crust, namely, limestone, marbles, dolomites, etc., and, as a result of organic activity, it is found in the shells of the crustaceans. The calcareous matters of the soil, that is, the carbonates of lime therein found, are of the highest importance from an agricultural point of view. They not only favor the process of converting nitrogenous bodies into forms suitable for plant food, but also exert a most potent influence on the physical state of the soil and its capacity for holding water and permitting its flow to the rootlets of the plant.

Sulphur occurs in nature in both the free and combined state. In the free state it is found in volcanic regions such as Sicily, Iceland and the Western United States. Its usual form of occurrence is in combination with the metals to form sulphides, or with oxygen and a metal to form sulphates. Sulphur and iron combine to form iron pyrites or iron disulphide (FeS_2), while sulphur, oxygen, and calcium are found in gypsum, an important fertilizing material.

Sulphur plays an important part in the nourishment of plants, being found in them both as sulphuric acid and in organic compounds; it is an essential constituent of both animal and vegetable protein and is thus intimately associated with one of the most important classes of foods.

Hydrogen is a colorless, invisible gas, without taste or smell. It occurs free in small proportions in certain volcanic gases, and in natural gas, but its most common form is in combination with oxygen as water (H_2O), of which it forms 11.19 per cent by weight. It also occurs in combination with carbon to form the hydrocarbons, such as the mineral oils (petroleum, etc.), and gases. Hydrogen is of no importance to agriculture in a free state, but water is the most important and necessary of all plant foods.

Chlorine occurs free in nature only in limited amounts in volcanic vents. Its most common form is in combination with hydrogen, forming hydrochloric acid, or with the metals to form chlorides. It combines with sodium to form sodium chloride or common salt ($NaCl$), which is the most abundant mineral ingredient in sea water and which can usually be detected in rain and ordinary terrestrial waters. In this form, also, it exists as extensive beds of rock salt, which is mined for commercial purposes.

Chlorine is found uniformly in plants and may be regarded as a common constituent thereof. Common salt applied to a soil modifies its power

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of attracting and holding water. Its further action has already been explained.

Phosphorus never occurs in nature in a free state but exists in combination in greater or less quantities in all soils and in many minerals. Its combinations are also found in large deposits of mineral known as phosphorite, apatite and as so-called pebble and phosphate rock. Phosphorus in some sort of combination is one of the most essential elements in animal and plant food. In animals its compounds form almost all of the mineral matter of the bones, and in plants they are important constituents of the ash of seeds. It exists in organic combination both in animal and vegetable tissue as lecithines and other compounds.

Nitrogen as a mineral constituent of soils, is found chiefly in the form of nitrates, but owing to their solubility, they cannot accumulate in soils exposed to heavy rainfalls. The gaseous nitrogen in the soil is also of some importance, since it is on this material that the organisms which have a symbiotic activity with the rootlets of some plants probably act in the process of the fixation of atmospheric nitrogen in a form accessible to plants. Nitrogen in the free state, it is believed, is not directly absorbed into the tissues of green plants. It is necessary that it be oxidized in some way to nitric acid or some compound containing it before it can be assimilated. The importance of nitrogen as a plant food has been already described.

Boron occurs chiefly in volcanic regions, but is much more widely distributed in the soil than was formerly believed. It is a constituent of the ash of many plants, and is thought by some to be a true plant food. A more reasonable theory is that its presence in vegetable products is a mere incident to its occurrence in the soil. It is one of the least abundant of the elements, not occurring in sufficient quantity to find a place in our investigation. Boric acid and borax are used to some extent as a preservative.

Fluorine does not occur free in nature, but it exists chiefly in combination with calcium, forming fluorspar, traces of which are found widely distributed. In combination chiefly with lime it occurs in bone and many other substances. It is one of the elements which does not combine with oxygen, and can be isolated only with the greatest difficulty. At most, very small traces of it are found in soils. Fluoride of lime is found, however, in considerable quantities in certain phosphate deposits.

Aluminum is, probably, next to oxygen and silicon, the most abundant element of the earth's crust, of which it is estimated to form about one-twelfth. It has never been found, in nature, in the free state, but commonly occurs in combination with silicon and oxygen, in which it is an abundant constituent of feldspar, mica, kaolin, clay, slate, and many other rocks and minerals.

By the weathering of feldspar, mica, and other

minerals containing aluminum, true clay is formed, which is of the greatest importance in the constitution of the soil. The compounds of aluminum are not important as plant food except when they contain potash but they form valuable constituents of the soils, furnishing a large part of its bulk, and modifying in the most profound degree its physical properties. It is the custom of some to use the word clay to designate the fine particles of soil which have, in general, the same relations to moisture and tilth as the particles of weathered feldspar, etc. In a strict chemical sense, however, the term clay is applied only to the silicates of alumina and the silica found therewith formed. The fertility of a soil is indirectly dependent on the quantity of clay which it contains, its relations to moisture and amenability to culture being largely conditioned upon its clay content. The determination of the percentage of clay in soils is an operation of the highest utility in forming an opinion of the value of a soil based on physical data alone.

Calcium is one of the commonest and most important elements of the earth's crust, of which it has been estimated to compose about one-sixteenth. It does not occur free in nature, but its most common condition is in combination with carbon dioxide, forming the mineral calcite, marble, and the very abundant limestone rocks. In this form it is slightly soluble in water, especially when containing carbon dioxide, and

hence lime is very generally found in natural waters, in which it constitutes the chief ingredient necessary for the formation of the shells and skeletons of the various species of mollusca and corals. In combination with sulphuric acid calcium forms the rock gypsum and other forms. Lime is not only a necessary plant food, but also influences in a marked degree the physical condition of the soil and the progress of nitrification. Many clay soils are rendered porous and pulverulent by an application of lime, and thus made far more productive. The sourness or acidity of soils is also corrected by the application of lime. Although existing in great abundance, it has not commanded the degree of attention from agriculturalists which its merits deserve. It forms an essential ingredient of plants and animals, in the latter being collected chiefly in the bones, while in plants it is rather uniformly distributed throughout all the tissues. Both in common language and in chemistry the term lime is applied to the product of burning limestone (carbonate of lime) until the carbon dioxide is expelled. In the freshly burned state, lime contains no water. When exposed to the air it gradually absorbs water and carbon dioxide, which enter into chemical combination, forming air-slaked lime. Lime is changed into slaked lime with great rapidity and with the evolution of much heat on the application of water.

Magnesium occurs chiefly in combination with silica and carbon dioxide or with lime and carbon

dioxide in the mineral dolomite. It is intimately associated with calcium and a trace of it is nearly always found where lime occurs in any considerable quantity. The bitter taste of sea water and some mineral waters is often due to the presence of salts of magnesia. In combination with silica it forms an essential part of such rocks as serpentine, soapstone, and talc. Magnesia is useful, especially in the formation of seeds, but it is not absent from other parts of the plant. It performs its functions best in the presence of calcium compounds and in the absence of the latter magnesia salts may easily be injurious.

Potassium combined with silica is an important element in many silicates as, for instance, orthoclase. Granite rocks usually contain considerable quantities of potassium, and on their decomposition this becomes available for plant food. In the form of chloride, potassium is found in small quantities in sea water, and as a nitrate it forms the valuable salt known as niter or saltpeter. Potassium, as is the case with phosphorus, is universally distributed in soils, and forms one of the great essential elements of plant food. Under the form of kainite and other minerals large quantities of potassium are used for fertilizing and for the manufacture of pure salts for commercial and pharmaceutical purposes. The ordinary potassium salts are very soluble and for this reason they cannot accumulate in large quantities in soils exposed to heavy rainfall. In the

form of carbonate, potassium forms one of the chief ingredients of hard-wood ashes, and in this form of combination is especially valuable for fertilizing purposes; potash salts, being extremely soluble, are likely to be held long in solution. Some of them are recovered in animal and vegetable life, but the great mass of potash carried into the sea still remains unaccounted for. The recovery of waste of potash is chiefly secured by the isolation of sea waters containing large quantities of this salt and their subsequent evaporation. Such isolation of sea waters takes place by means of geological changes in the level of the land and sea. In the raising of an area above the water level, there is almost certain to be an enclosure, of greater or less extent, of the sea water in the form of a lake. This enclosure may be complete or only partial, the enclosed water area being still in communication with the main body of the sea by means of small estuaries. If this body of water be exposed to rapid evaporation as was doubtless the case in past geological ages, there will be a continual influx of that evaporated. The waters may thus become more and more charged with saline constituents. Finally a point is reached in the evaporation when the less soluble of the saline constituents begin to be deposited. In this way the various formations of mineral deposits, produced by the drying up of enclosed waters takes place.

Sodium is never found free in nature, but its

most common form is in combination with chlorine as common salt, an important ingredient of sea water. Combined with silica sodium is an important element in many silicates. Sodium, although closely related to potassium chemically, cannot in any case be substituted therefor in plant nutrition. While it is certain that plants can thrive without a trace of sodium, it is believed to be helpful in some cases, and its salts may replace those of potassium in so far as osmotic and neutralizing functions are concerned. In combination with nitrogen it forms soda (or Chile) saltpeter which is a valuable fertilizer on account of its content of nitric acid.

Iron is the most abundant of the heavy metals, and occurs in nature both free and combined with other elements. In the free state it is found only to a limited extent in basaltic rocks and meteorites, but in combination with oxygen it is one of the most widely diffused of metals, and forms the coloring matter of a large number of rocks and minerals. In this form, too, it exists as the valuable ores of iron known as magnetite and hematite. In combination with sulphur it forms the mineral pyrite, FeS_2 . The yellow and red colors of soils are due chiefly to iron oxides. Iron salts are essential to the production of chlorophyll, the coloring matter in leaves, and to its functional activity. Iron is one of the essential constituents of the hæmoglobin, or red coloring matter therein, without which oxygen could not

be properly carried to every part of the animal body.

Titanium is apparently of no importance in plant nutrition, but its occurrence in many soils requires notice. It has been found to be one of the most widely distributed elements.

Manganese, next to iron, is the most abundant of the heavy metals. It occurs in nature in combination with oxygen, in which form it is associated in minute quantities with iron in igneous rocks or in the forms known mineralogically as pyrolusite, psilomelane and wad. As the peroxide of manganese it occurs in concretionary forms scattered abundantly over the bottom of the deep sea. It is found in the ash of some plants, but is not believed to be essential to plant growth.

Chromium in so far as known takes no part in plant nutrition and its occurrence in the soil is only of importance from an analytical and color standpoint.

Barium occurs in nature combined with sulphuric acid, forming the mineral barite, or heavy spar, or with carbon dioxide forming the mineral witherite. It is of small importance from an agricultural standpoint.

CHAPTER III

THE RELATION BETWEEN SOILS AND FERTILIZING MATERIALS

Exhaustible Elements and Non-exhaustible Elements—
Preference Shown by Plant Life—Separate Fertilizing
Ingredients—Economy in Separate Ingredients.

A MANURE is a substance designed to supply one or more of the essential constituents of plant food, and, where necessary, to improve the physical condition of the soil to which it is applied. The essential constituents of plant food must contain the elements carbon, hydrogen, oxygen, nitrogen, phosphorus, sulphur, potash, lime, magnesia, and iron and probably silicon, chlorine and sodium. Of these, carbon, hydrogen and oxygen, and some of the nitrogen are derived from air and rain, most of the nitrogen and the remaining elements being obtained from the soil. Almost every soil contains enough Ca, Mg, S, Fe, Si, Cl, and Na for the growth of a full crop, but nitrogen, phosphorus and potash are often present in but small quantity, and become exhausted by the removal of farm produce.

A general manure or fertilizer is usually understood to be the agency which can supply these three constituents, but inasmuch as some crops

either contain an excess of one or other of these, or are better able to obtain some one or other of them from the soil, than are other crops, it is frequently economical to apply a special manure to meet the needs of such crops. For what is known as to the requirements of individual crops a work on agricultural chemistry must be consulted. It thus happens that special manures are divided into phosphatic, nitrogenous, and potash manures. It is necessary, in order for a manure to be efficient, that it shall not only contain the requisite constituent or constituents of plant food, but that the nutriment shall be in an assimilable form, and it has been ascertained that in whatever condition the plant food may be actually absorbed, the absorption occurs the more rapidly the more soluble the food constituents of the fertilizer.

There is no way to tell, without experiment, what food constituents a soil lacks. The crops themselves give valuable suggestions. As a rule lack of nitrogen is indicated when plants are pale green in color, or when there is small growth of leaf or stalk, other conditions being favorable. A bright, deep green color, with a vigorous growth of leaf or stalk, is, in case of most crops, a sign that nitrogen is not lacking, but does not necessarily indicate that more nitrogen could not be used to advantage. An excessive growth of leaf or stalk, accompanied by an imperfect bud, flower, and fruit development, indicates too much nitrogen for the

potash and phosphoric acid present. When such crops as corn, cabbage, grass, potatoes, etc., have a luxuriant, healthful growth, an abundance of potash in the soil is indicated; also when fleshy fruits of fine flavor and texture can be successfully grown. On the contrary, when these plants fail of a luxuriant growth, or are very low grade in quality, it is certain indication that potash is lacking. When a soil produces good, early maturing crops of grains with plump and heavy kernels, phosphoric acid will not generally be found deficient in the soil.

In order to ascertain with greater certainty what food elements are lacking in the soil, careful experiments would have to be carried out on the soil and crops, by applying different kinds of fertilizing materials in different combinations, using, for example, potash compounds in one combination, phosphoric acid compounds in another, nitrogenous materials in another. Then different combinations can be made on other portions of the crop. Some portions of the field can be left without application of any kind. The result can then be studied in the yield of crop. In carrying on such field tests, several difficulties may be met. The season may frequently be such as to interfere seriously with the favorable action of the fertilizing materials applied. Thus, a severe drought may counteract all other conditions and prevent a satisfactory yield. The difference of mechanical condition of the soil on the same farm or even in

the same field may prevent a fair comparison of the action of different kinds of fertilizing materials and elements. But, notwithstanding such difficulties, valuable suggestions will be gained from an experimental study of the soil through the behavior of the crops.

It is a fact of great interest and importance that one form of a fertilizing constituent is preferred by some plants to the same constituent in another form. This preference is indicated by greater yield or better quality of product or by both. Thus, wheat seems to give better results when nitrogen is applied in the form of nitrate of soda than in any other form. The quality of tobacco is injured by potash in the form of muriate and, hence, only sulphate of potash should be used for fertilizing purposes. The quality of sugar beets and of potatoes appears to be better when sulphate of potash is used.

While the soil may contain quantities of fertilizer naturally, in most cases it will not pay to give serious attention to this source of fertilization. Nitrate of soda, when used alone should always be applied to growing crops, and for quick effects. For young fruit trees or for vegetables, one or more applications may be made with benefit. Complete fertilizers usually have a small proportion of their nitrogen in the form of nitrate of soda, and the remainder in a less active form, so that by the time the nitrate of soda is utilized, the nitrogenous products become effective.

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Sulphate of ammonia is a quick-acting nitrogenous fertilizer, but should be used only when the soil has been lately limed. All forms of potash are equally available, but should be applied as early in the season as possible; even fall applications are advisable, as there is little danger of loss through drainage. Lime also aids the effectiveness of potash salts. Phosphates in the form of superphosphate or acid phosphates are very quickly available, resembling nitrate of soda in this respect, though it is hardly advisable to make more than one application, early in the season or at planting time. All other forms of phosphates are best applied in the fall, or very early in the spring.

It will generally be found more economical to purchase fertilizing materials of high grade. In applying fertilizers, bulk is often desirable, but in purchasing commercial fertilizers, the object should be to secure as much nitrogen, potash and phosphoric acid in available form as possible, for one dollar, instead of as many pounds as possible of fertilizers, regardless of the amount of plant food contained in it. This is particularly applicable to mixed fertilizers. Since there is a smaller bulk to handle in mixing, a smaller number of packages for holding and, consequently, less weight and freight, it is, as a rule, more economical to purchase fertilizers in their more concentrated forms. For illustration, it is more economical to purchase one ton of high-grade fertilizer than

three tons of a low-grade fertilizer, one ton of the former containing the same amount of plant food contained in three tons of the latter; because, in making the latter, three times as many packages or bags are required and three times as much freight must be paid all for the same amount of plant food.

Fertilizers cannot, as a rule, be in too finely powdered condition nor can they be too dry. With many materials, bone, for example, the availability as plant food is directly dependent upon the fineness of division. Excessive moisture in fertilizer is undesirable on several grounds. First, the larger the amount of moisture, the smaller will be the amount of plant food in a ton. Second, excess of moisture causes the particles to stick together, and is likely to result in caking and clogging when used in drills. Third, an excess of moisture favors the decomposition and loss of nitrogen in many forms of organic matter. This is shown by the fact that some fertilizers give off a very offensive odor if allowed to become damp, while they are comparatively free from disagreeable odors if they are thoroughly dry. A strong odor in a fertilizer is an indication that organic matter is decomposing and nitrogen is being lost.

Materials which are readily soluble can be scattered over the surface. After the first rainfall they distribute themselves throughout the soil very completely and uniformly. Such materials are nitrate of soda, sulphate of ammonia, soluble

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phosphates and soluble potash salts. Fertilizers which dissolve easily and diffuse through the soil rapidly and which are not readily retained by the soil, are best applied only when the crops are ready to utilize them. If put on too early, there is danger of their leaching from the soil and being carried away beyond the reach of the plant, and thus lost. Hence, it is not wise ordinarily to apply guano, ammonia compounds or nitrate of soda in the fall, except in climates which have a dry fall and winter. Their application should be deferred until spring. In wet springs, ammonia compounds are preferably applied rather than nitrate of soda; or, if nitrate of soda is used, loss may be avoided by making several small applications instead of one at the start.

In applying highly concentrated commercial fertilizers, it is wise to prevent the fertilizer coming in contact with the seeds or foliage of plants. Fertilizers containing ammonia compounds should not be mixed with wood ashes, lime, or Thomas slag (odorless phosphate), since some of the ammonia is likely to be lost.

CHAPTER IV

PEBBLE PHOSPHATE ORE DRESSING AND MILLING

Steam Shovels and Hydraulic Mining Practice

FLORIDA phosphates, classed as hard rock, soft rock, land pebble, and river pebble, are found in the Eocene, Miocene, and more recent geological formations. The hard-rock phosphates occur massive, laminated, and as boulders piled together, also in the form of pebbles where the other rocks have been broken by weathering and water movements. This kind of material possesses a variable structure from compact to fibrous, and while usually of a creamy color is frequently stained with iron oxide.

The soft rock occurs in deposits by itself and associated with hard rock phosphate. It may be clayey or sandy and fill spaces between boulders of hard rock phosphate. It is evidently a secondary deposit formed by the disintegration of other phosphates of lime.

It carries from 20 to 30 per cent less phosphate of lime than hard rock phosphate, which varies from 80 to 85 per cent.

Land-pebble phosphate is essentially a mass of whitish phosphate pebbles varying in size from

grains to 1 in. in diameter, averaging possibly a little over $\frac{1}{4}$ in. They are hard and have usually a matrix of phosphate clay and sand. The percentage of phosphate of lime which the pebbles contain is from 75 to 80, but the average material as mined would not reach this standard. This ore is mined open cut, by dredging, and by hydraulicking; it is then washed, dried, and shipped to fertilizer works, mostly abroad.

River-pebble phosphates are found as bars in the rivers of southern Florida, and with them are found the fossil remains of vertebrates. The river pebble is blue or black, varying from 1 in. downward in size, and frequently occurring as the hardened casts of small molluscs. The percentage of phosphate of lime in the river pebbles is between 58 and 68; at present river dredging for phosphate pebbles is not as active as the mining operations for land pebbles.

Florida phosphate beds are covered with soil to varying depths, which is removed by means of steam shovels or hydraulic nozzles. If the deposits are below water level, traction dredges working on the land, or floating dredges, are used.

The overburden of land deposits is stripped from the ore by steam shovels, a cut being taken the full swing of the shovel boom, and the shovel moved forward a short rail length when this is finished.

The capacity of the dipper or shovel varies from 1 to $2\frac{1}{2}$ cu.yd., and the boom and dipper arm is

made to conform to the depth of the alluvions. For example, a 35-ft. boom will raise material 18 to 20 ft. above the shovel track and make a cut 35 ft. wide. The cars to carry the overburden are standard gauge of 12 cu.yd. capacity. They are usually dumped by hand, although some of the more recent cars have air-dumping arrangements which are controlled from the engine cab. The cars are run out to the dump and handled in the usual manner, care being taken not to waste the material where it will cover future work. Steam shovel work is done by contract, the price being 20 cents per cu.yd.

Whenever conditions are favorable and space available for the disposal of the material, the overburden is removed by the hydraulic method, and pumped into an abandoned excavation from which the phosphate ore has been removed. The cost of stripping by the hydraulic method is from 5 to 8 cents per cu.yd. The overburden in Florida phosphate fields is favorable for this kind of work, being clean, fine sand, with some pebbles, the majority of the foreign substances being sods, stumps and palmetto roots. Occasionally the sand is cemented and grades into a soft, but tough, sandstone which must be blasted before hydraulicking. Owing to the overburden containing little clay, it can be stacked in large dumps that do not liquefy and run into the streams.

In Florida where hydraulic stripping is practiced, hydraulic mining may be also, in which case

the material is broken by playing one or more streams of water under a pressure of from 90 to 140 lb. per sq.in. against the face of the deposit. This operation causes the rock containing the phosphate to crumble and flow into a ditch cut in the underlying marl. The flow is aided at times by additional water from a $\frac{1}{4}$ -in. nozzle ditch hose, the object being to drive the material into a sump about 8 ft. square cut in the marl. From the sump the material is lifted by an 8-in. or 10-in. centrifugal pump and discharged into the washers. Since the rock material consists of firm sand and round phosphate pebbles, very little of it being over $1\frac{1}{4}$ in. in diameter, it is easily made to flow through the ditch into the sump, on a grade of 2 in. to the foot, by the use of about ten times its weight of water.

The hydraulic nozzles are connected to the main water supply pipe which is usually 10 in. in diameter. Where two nozzles are worked each has from 200 to 500 ft. of 6-in diameter, flanged, spiral-riveted, galvanized water pipe. Asphalt roofing paper or tar board is used for flange gaskets. At one or two convenient places, in this 6-in. line, a ball-and-socket joint is applied to facilitate the lateral movements of the nozzles.

When two nozzles are used they are pointed so as to wash the material to a central point, which is the ditch leading to the sump. In case the ditch clogs, an auxiliary hose is coupled just back of the nozzles and the flow of water from this is

used to move the material to the sump. After the face of the rock is mined so far away from the sump that the material does not flow properly through the ditch, a new sump is blasted 50 to 75 ft. nearer the working face, and the pump is moved to it. The pressure required for hydraulic mining of this kind is not high, but the work demands a large volume of water in order to transfer the material through the ditch to the sump and not choke the pump by an excess of solids.

The outfit for transferring the ore to the washer consists of a centrifugal pump of the volute box type, with chilled cast-iron facing, directly connected to the slip-ring motor. The tail-piece of the pump, which must be flexible, is raised from the sump by means of a set of triple blocks suspended from a tripod. This arrangement is necessary, because whenever the mouth of the suction pipe becomes clogged with grass, roots, etc., it must be raised out of the water for cleaning. In case the distance is more than 800 to 900 ft. between the mine pump and washer, a relay pump is usually installed. In such cases the mine pump discharges into a sump from which the relay pump draws its material and forces it to the washer. This method is used owing to the difficulty arising from back flow and water hammer when operating two centrifugal pumps in series. Where the centrifugal pump discharges without much head, the end of the pipe line is elevated for a pipe length at an angle of 45° in order to furnish suf-

ficient pressure head to work against and prevent vibrations in the pump.

After the material reaches the washer from the mines it is delivered to a relay pump without going into a sump. This pump lifts the material to the top of the washer, where it is discharged into a launder that feeds a rotary screen having $1\frac{1}{4}$ -in. holes. The screen makes two products; an oversize consisting of mud balls and coarse rock which is sent directly to the tailing pond, and an undersize which is discharged on to an inclined stationary screen with $\frac{3}{4}$ -in. slop openings, where some of the sand is removed, the operation being assisted by sprays of water. The oversize from this screen passes to a 16-ft. double log washer which discharges the material into another 16-ft. single log washer. These logs separate the particles of phosphate, sand, and pebble from the silica by reason of their grinding and mixing action. Wash water is also supplied to the logs, which assists the separation by moving the silica sand backwards and over the tail-gate of the log-box. The last set of logs discharges on to a shaking screen which further eliminates all but about 6 to 8 per cent of the remaining silica and the greater part of the water. The dewatered material from this screen goes directly into a hopper-bottom storage bin over the railroad tracks, where it is ready for transportation.

CHAPTER V

HARD ROCK PHOSPHATE ORE DRESSING AND MILLING

Loss of Soft Ores—Separating the Ores from Clays, etc., and Process of Roasting or Drying

THAT there is considerable loss of phosphate in mining is well known. Practically all the deposits contain, with other material, more or less phosphate in a soft or pulverulent condition. Under present methods of mining and treatment this "soft" phosphate is necessarily lost in the process of washing, being carried to the dump along with the sand, clay, and other constituents of the matrix. The amount of phosphate thus discarded may be expected to vary with different deposits and under different conditions. After reaching the dump there is more or less mechanical separation so that samples taken from one part of the dump may be found richer in phosphate than from some other part of the same dump. Samples taken at random by the writer and analyzed, from some phosphate dumps in the hard rock region gave the following analyses: Total phosphoric acid, 9.99 to 12.14; which is equivalent to tricalcium phosphate, 21.81 to 26.50. In an-

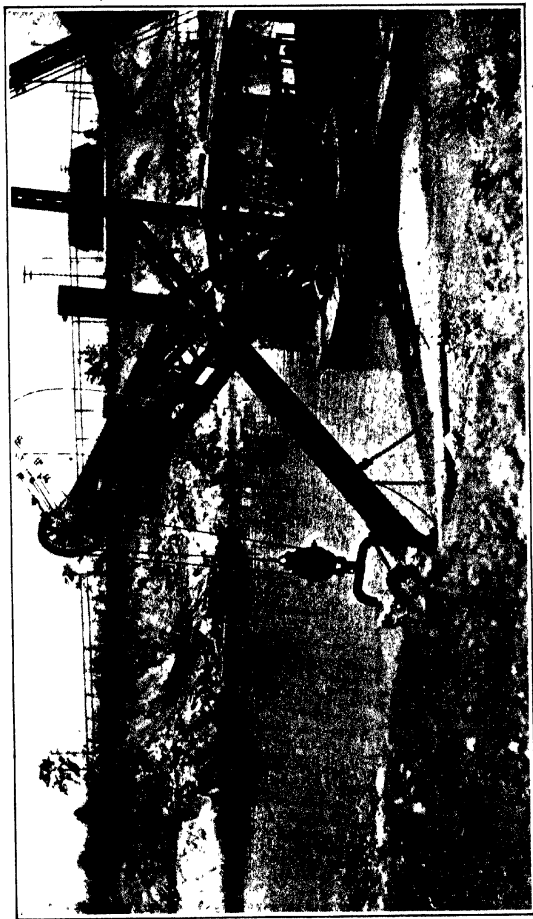


FIG. 1.—Dredge-boat Dredging in Phosphate Ore. Dipper in Act of Taking up a Load for Skip-car.

other case, a sample of floats from the dumps in the land pebble section gave as follows: total phosphoric acid, 11.47; equivalent to tricalcium phosphate, 25.04. In still another analysis made of the plate-phosphate ore, it was as follows: silica, 58.95 to 60.10; iron and alumina, 11.70 to 11.20; calcium phosphate 26.80 to 27.92. It is estimated in this particular case that approximately four tons of material was excavated and washed in order to obtain one ton of the high grade rock phosphate (77 per cent). From this it is evident that of the material taken from the pit three-fourths, carrying about 27 per cent calcium phosphate, goes to the dump, while one-fourth, carrying 77 per cent calcium phosphate, is saved; thus of the total phosphate ore taken from the pit, in this instance at least, one-half goes into the dump.

From these data it is apparent that a large amount of phosphate ore is being lost annually in this section and that any economical method of reclaiming this waste or of utilizing the floats, if such be devised, are clearly of the greatest importance to the phosphate industry, and ultimately to the agricultural interests of the whole country.

With the extension of agriculture necessary to support increased population, together with the progressive exhaustion of the new and naturally rich soils, there arise increased demands upon the phosphate supply. At the present this demand is coming mostly from the older countries of Europe, and the phosphate now produced is largely ex-

ported. The time is not far distant, however, when an equally strong demand will come from the exhausted soils of our own country. The hydraulic and steam-shovel methods of stripping the overburden and the mining of rock, to a certain extent, is described in Chapter I of this work. In the pits in the hard rock section, steam dipper dredges are used, which load the skips that are hauled up an incline and delivered to the top of the washer. The phosphate ore thus carried from the pits is dumped upon "grizzlies," where it is sized. That which passes through the bars of the "grizzlies" is ready for sizing by the "separator," or trommel, but that which is too large to pass through the bars is broken by hand with a pick, axe or dynamite and made ready to pass through the bars of the grizzly. The ore passing into the "separator" is sized for the first time for the set of double log washers where it receives its first treatment for the removal of the clay which adheres to the phosphate material. That part of the ore which is too large to pass through the perforations of the revolving screen, passes out the lower end and falls into a roll-jaw crusher and after being crushed it falls through a chute into the first set of log washers where it is washed with ore which has been sized by the revolving screen or trommel. In the log washer, one end of the washer revolves in a gudgeon placed below the water in the box containing the ore to be washed; the other end works in journals. The

log, which is driven by gear-wheels, works the ore towards the head of the box and discharges it into the second washer which is a single log. Water is introduced at the upper end of the box, while the ore is fed at the lower end; the clean water thus meets the ore and when it becomes dirty it flows out at the lower end, carrying with it the clay in suspension. There is no general standard for these log washers. The box is about four feet deep at one end and two feet at the other, according to the length of the logs, which vary from sixteen feet to thirty feet and are pitched at an angle sufficient to give a rise of one and one-quarter inches to the foot. The dirty water from the washers generally flows away in sluices, but where the fall is not sufficient a centrifugal pump of some type is used to assist in its removal.

After the log washers have removed most of the clayey matter, the ore passes through a chute into a trommel with an internal spray, which eliminates the remaining clay and the smaller portions of the sand from the ore. These screens have jackets ranging from one-eighth inch to one-sixteenth inch, and are commonly known as "rinsers." The ore after passing through the "rinser," falls through a chute on to a slowly revolving table, known as a "picking-table," where boys and old men pick out the "sand rock" and other foreign matter not removed by the log washers and screens. The ore after hand-sorting is automatically pushed through the center of the table by a large brush or scraper

into a chute leading to a car under the picking-table, in which it is carried to the drying shed,

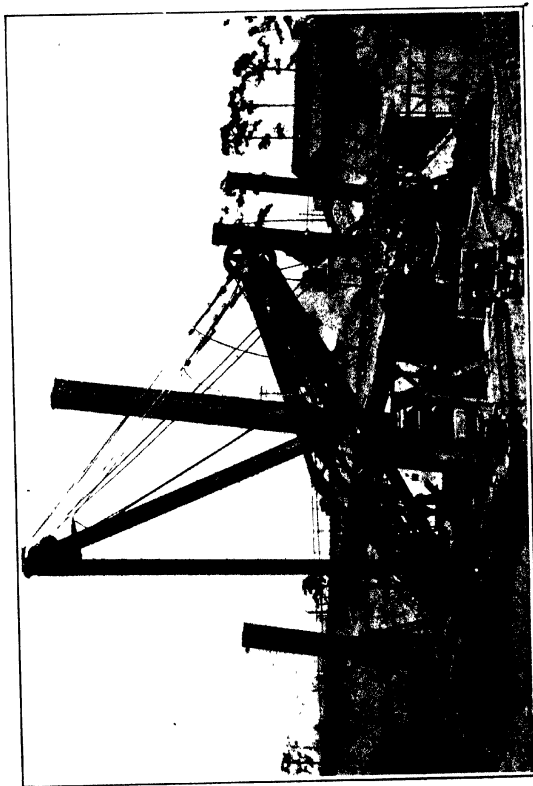


FIG. 2.—Floating Dredge-boat in Mine Pit Emptying a Dipper of Phosphate Ore in Skip-car on Incline Track to be Transported up Incline Track to Washer.

where it is kiln-dried before being loaded into the railway box cars for transportation.

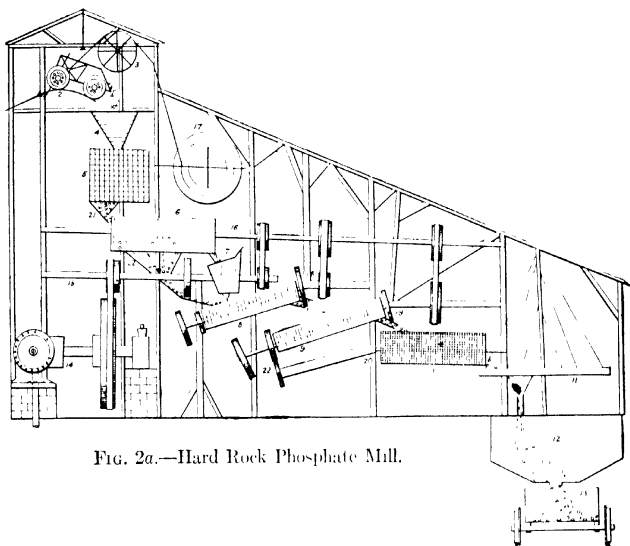


FIG. 2a.—Hard Rock Phosphate Mill.

DETAILED DESCRIPTION OF FIG. 2a

No. 1, incline track running from the phosphate pits up the top of the washer upon which the crude ore is hauled in the skip-cars.

No. 2, skip-car delivering a load of phosphate ore to the grizzle bars.

No. 3, pulley or sheave at the top of washer upon which runs the wire cable that hauls the skip-car up the incline track.

No. 4, grizzle bars upon which the ore is dumped and where it receives its first sizing, and is forced through and broken up before falling into the separator.

No. 5, chute from bars to separator.

No. 6, separator which sizes the rock for the first set of double log washers. That which passes out of the separator falls in

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the crusher, and is crushed for the log washer when too large to pass through the separator.

No. 7, crusher which crushes the rock for the log washers

No. 8, first set of double log washers.

No. 9, set of single log washers where the rock goes after passing through the set of double log washers.

No. 10, rinser which gives the rock its final washing before depositing upon the picking tables where it is picked by hand.

No. 11, circular picking table upon which the rock is picked.

No. 12, ore bin where rock is dumped after being picked on picking table.

No. 13, mine car that receives ore from the bottom of the ore bin through a chute, and is used to carry the ore to the drying sheds, where it is burnt before loading upon the railroad cars for transportation.

No. 14, 200 H.P. engine horizontal type, for driving machinery.

Nos. 15 and 16, line shafts for pulleys and belting.

No. 17, hoisting drum for hoisting skip-cars from pits up to the washer to dump the wet, crude ore on bars for treatment.

No. 18, universal joint connecting shafts of log and line shafts as all log washers have to be inclined to allow water to run down through them to thoroughly wash ore.

Nos. 19 and 20, other universal joints in shafting.

No. 21, chute for sliding ore into separator.

No. 22, gearing of the log washers.

To reduce the moisture to the required 3 per cent the producers of land-pebble phosphates use mechanical dryers entirely. While there are several kinds of these dryers, all are of the rotary-cylinder type; that is, heated air and gases of combustion are made to pass through the cylinder from a furnace. The wet phosphate ore is fed automatically into the cylinder and by means of shelving

riveted to the sides of the cylinder is gradually worked from the cold to the hot end, being repeatedly showered through the hot gases in its passage until discharged. The fuel is coal, wood, or crude petroleum.

The excess of moisture in the hard rock in this section of Florida during the early years of mining was removed entirely by kiln burning, a process still in use by many operators. For this purpose the phosphate ore is placed on ricks of wood. The wood is then fired, and the phosphates partly smothering the flames permits slow burning, and by the gradual spread of heat, the phosphate becomes more or less uniformly dried. More recently, with the growing scarcity of wood in the hard-rock section several large producers have installed mechanical dryers similar to those used by the land-pebble miners. In a number of instances the mechanical dryers are in different parts of the country, and away from the actual mining operations.

CHAPTER VI

PHOSPHORUS

Origin of Phosphate Rock, Basic Slag, Bone Meal, Ammonium Sulphate, Sodium Nitrate, Organic Nitrogenous Materials, Potash and Guano.

It is a well-known fact that phosphorus is an element and like the element iron, is almost universally distributed over the globe, and is found in all living things. Therefore, it is reasoned that it may like iron, be accumulated in large beds by natural law which governs the concentration of mineral masses. Again it is suggested that phosphoric acid, derived from mollusca, deposits from birds, fish and saurians, has filtered down and replaced the carbonic acid in the underlying limestone, converting it into phosphate of lime. It is true that in many instances the phosphate of lime very rarely contains any trace of organic remains, while the limestone on which it rests abounds in the casts of mollusca in some sections of the Southern States. Then again, in proximity to the hard rock phosphate is a soft phosphate of lime that has the consistency of soft plastic clay. This soft phosphate often underlies the hard rock and is several feet in thickness. This condition prevails in the hard rock phosphate section of Florida.

Speaking of phosphates in general, however, the fact has been noted that within the rain belt, when

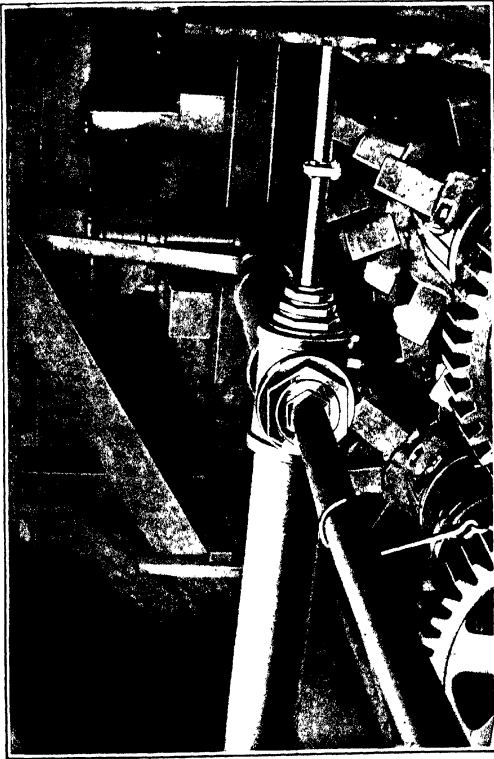


Fig. 3.—Double Log Washer Showing Water Pipe and Connections.

guano deposits rest upon limestone the phosphoric acid is leached out and transforms the carbonate of

lime to phosphate of lime. An instance of this is cited in which limestone in one of the South Pacific islands was believed to have been changed to phosphate to a depth of several feet within a period of twenty years. The phosphoric acid in this instance was leached by rainwater from recently deposited guano. The belief has been expressed that the phosphoric acid of the phosphates has been derived directly from bird guano. The local character of the bird rookeries determines the local occurrence of phosphate rock.

Whether the hard rock phosphates of Florida resulted from a superficial and heavy deposit of soluble guano, or from the concentration of phosphate of lime already widely and uniformly distributed throughout the mass of original rock, or from both of these sources is regarded as a difficult question. The writer does not believe, however, that the bird-guano theory will account for these widely disseminated phosphates any better than for the intensely localized hard rock phosphates. The key to the solution of the hard-rock phosphate problems is found, in the writer's opinion, in a study of the geological history of each particular section of the world's deposits.

However, the evidence of the formation of phosphate by the transformation of carbonate of lime into the phosphate of lime is entirely incontrovertible, since many of the boulders retain the original calcareous shells now phosphatized. The evidence of subsequent secondary deposition in the cavities

is likewise obtained from the structure of the rock itself. This condition is observed in the hard-rock section of Florida.

Basic Slag.—It has been found within recent years that the phosphatic slag from the basic process of steel-making possesses considerable value as a fertilizer. The content of phosphoric acid varies from 10 to 25 per cent, and, according to some, the phosphoric acid exists as calcium phosphate. The slag is, however, of little value as a manure unless it be very finely ground—e.g., 80 per cent of it should pass a sieve having 100 meshes per linear inch. The attainment of this condition constitutes the preparation of the slag for the market, and is expensive on account of hardness of the material. Grinding is commonly performed by a ball mill which consists essentially of a drum, the inner surface of which is polygonal; the drum contains a number of cast-steel balls of various sizes. Rotation of the drum breaks up the slag by the rolling and percussive action of the balls, and the comminuted material is systematically separated by sieves in the sides of the drum. The sieves which effect the final separation are protected from direct contact with the balls by perforated iron plates.

Bone Meal.—This is of manurial value on account of its phosphates, but it also contains nitrogenous matter. Fresh bones contain about $\frac{2}{3}$ per cent of nitrogen; they decompose very slowly when used as a manure. When the bones are

previously fermented in heaps, the nitrogenous matter becomes more readily assimilable.

Bones are also more available as manure when they have been steamed for the removal of fat. Boiled bones which have been passed through the glue-maker's hands contain a smaller proportion of nitrogen than do raw bones. The boiled bones can be more finely ground and divided than is represented by the condition of bone meal; the fine product is known as bone flour. Dissolved bones is the product of the treatment of bones with commercial sulphuric acid.

Ammonium Sulphate.—This is produced as a by-product in the destructive distillation of coal. The working up of gas liquor for ammonium sulphate is carried out in the following manner: The liquor is heated to drive off the free ammonia and the vapor is absorbed in sulphuric acid, forming ammonium sulphate, which crystallizes and is periodically fished out. It is the common practice in some countries to use only that part of the ammonia which is liberated on distilling the gas liquor a'one, but sometimes the fixed ammonia is liberated by the addition of lime. Pure ammonium sulphate contains 21 per cent of nitrogen, corresponding to 25.75 per cent ammonia, and is a colorless salt. The commercial product varies in color from gray to brown, owing to the presence of tarry matter, and is sometimes yellowish from the presence of arsenic; this body is formed by the action of the hydrogen sulphide from the gas liquor

on the arsenic present in the sulphuric acid in which the ammonia is absorbed. Commercial ammonium sulphate usually contains about 24.5 per cent of ammonia. It should be free from ammonium sulphocyanide, which is a plant poison. This impurity is rarely present, save when the ammonium sulphate has been made by the direct saturation of gas liquor with sulphuric acid.

Sodium Nitrate.—Sodium nitrate is obtained from the deposits of crude nitrate in Chili and Peru. The deposits, which lie about six to ten feet below the surface, are known as caliche, and form a layer four to six feet deep. It is associated with clayey substances; the composition is, however, very various, and the content of sodium nitrate may reach 50 per cent.

The caliche is broken in a stone breaker, and systematically lixiviated in tanks heated by closed steam. Water being a rare commodity in nitrate districts, it has to be used for repeated extractions. When the liquid reaches a specific gravity of 1.55, it is run into crystallizing vats, in which it remains from four to six days; the mother liquor is then run off, and used for the recovery of iodine. The iodine characteristically present in crude nitrate probably exists as iodate. As much as 1 per cent of perchlorate is also found in some samples of caliche, and lowers the value of the latter considerably, since even small quantities of perchlorate are injurious to plants. The nitrate deposited after having been sun-dried has the following com-

position: sodium nitrate 96.75 per cent; sodium chloride 0.75 per cent; sodium sulphate 0.30 per cent; insoluble matter 0.10 per cent; water 2.10 per cent.

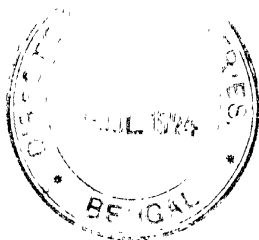
Organic Nitrogenous Materials.—Dried blood obtained from slaughter-houses is a type of these. It contains from 9 to 12 per cent nitrogen. Ground hoofs and horns form another manure of this class, as also waste woolen material, such as shoddy running from 5 to 8 per cent nitrogen.

Potash.—Potash, a necessary constituent of plant food, has been supplied mainly as one or the other of the products obtained in the Stassfurt mining industry of Germany. The chief salts are kainit, containing 12 to 14 per cent of potassium oxide; the double sulphate of potassium and magnesium, containing 27 to 28 per cent potassium oxide, which is obtained from kainit; carnalite with about 11 per cent of potassium oxide in the crude mineral; and crude potassium chloride of a strength corresponding to about 50 per cent potassium oxide. Magnesium salts and chlorides detract to some extent from the manurial value of these substances.

Guano.—This is the excrement of sea birds in a more or less altered condition. A distinction is drawn between nitrogenous and phosphatic guanos; the former are either of recent origin, or have not been subjected to weathering which is the case in such dry climates as that of Peru; the latter

(found in Australasia) have been so washed by rain as to contain little or no nitrogen.

Dry Peruvian guano contains its nitrogen in the form of uric acid and urates; when these have undergone partial decomposition, the guano becomes damp and contains ammonium carbonate, to fix which a "dissolved" guano is made by treating with sulphuric acid, the ammonia being converted into ammonium sulphate and the calcium phosphate rendered soluble. An "equalized" guano is a Peruvian guano in which the percentage of ammonia has been brought up by suitable admixtures.



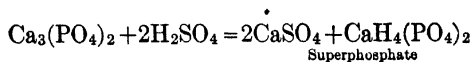
CHAPTER VII

ARTIFICIAL MANURE MANUFACTURE

Phosphatic Manures—Mineral Phosphates—Superphosphates
—Precipitated Phosphates—Mixed Manures.

THE only abundant form in which phosphorus is found, is as the various forms of calcium phosphate, and, to a smaller extent, as aluminium and iron phosphates. Of these, the calcium phosphates can better supply phosphorus to the plant than can iron and aluminium phosphates, probably because of the greater ease with which this compound is dissolved by feeble acids, e.g., carbonic acid, and by saline solutions. Deposits of calcium phosphate are widely distributed. The most definite mineral containing calcium phosphate is apatite.

Phosphates, even when very finely ground, are but slowly assimilated by plants, and are, therefore, almost exclusively used for making superphosphate, the process consisting in treating them with sulphuric acid in order to realize the following equation



as nearly as is practicable, $\text{CaH}_4(\text{PO}_4)_2$ being soluble in water. Calcium carbonate, a common impurity in phosphates, consumes sulphuric acid in this treatment. Other objectionable impurities in phosphates are the ferric oxide and alumina, because both oxides form insoluble phosphates, so that the proportion of soluble phosphates in the prepared superphosphates is diminished by their presence. Various plans have been proposed for removing calcium carbonate—e.g., treatment with an aqueous solution of CO_2 or SO_2 in which calcium carbonate is soluble; or by causticising the lime by heat, and acting upon it with ammonium salt—e.g., the chloride—the ammonia being recovered. Redonda phosphate (essentially AlPO_4) has been converted into an available form by treatment with sulphuric acid, yielding aluminium sulphate and phosphoric acid, or by heating with sodium chloride and superheated steam, whereby a portion of the phosphoric acid is converted into sodium phosphate.

“Superphosphate” is a mixture of calcium sulphate as gypsum with the acid phosphate of lime $\text{CaH}_4(\text{PO}_4)_2$ which is the essential manurial constituent. The crude calcium phosphate to be converted into superphosphate should be, as stated above, as free as possible from iron and aluminium compounds (not more than 3 per cent of $\text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3$) and from calcium carbonate. The material is ground very finely—e.g., to pass a sieve having 80 meshes per linear inch—and is

charged intermittently in 4 to 5 cwt. lots into a mixer composed of a lead-lined wooden tank, provided with an agitator, where it is mixed with chamber acid (vitriol of specific gravity 1.53 to 1.61, containing 62.53 to 69.43 per cent H_2SO_4), run in as required from an adjacent tank. The quantity of acid needed varies with the composition of the phosphate, 13 to 18 cwts. per ton of phosphate being the usual limits. The mixer is built above a brick chamber known as the "pit" or "den," and into this the semi-fluid mass, after it has been agitated for a few minutes, is discharged through a chute. The temperature of the mass in the pit rapidly rises to 110°C . Much gas is evolved (CO_2 , HCl , and HF), and solidification sets in. The gases are drawn off through flues, and pass through a scrubber, necessary on account of the objectionable character of HCl , and still more of HF . When the pit is nearly full, one of the sides, which is of wood and removable, is taken down and the product dug out and passed through a disintegrator, whereby it is reduced to powder. When mixed manures are being made, potash salts and nitrogenous materials are mixed during passage through the disintegrator.

In mixing and making of fertilizers, it was first proposed to make the ingredients correspond to the analysis of the plant. This method was practiced for some time, but it was found that there was already in the soil more or less available plant food and that fertilizing material was often applied

where one or more constituents could be omitted or reduced in quantity. It was then suggested that soil analysis should form the basis of determining the needs of the soil for different crops, but this failed to produce satisfactory results. The formulas at present used by many have been based, in part, upon the composition of the plant, and, in part, upon actual field tests.

The amount of nitrogen called for by analysis of plants is generally reduced because we can depend upon the soil to furnish a considerable amount. In case of leguminous crops, the amount of nitrogen which we need to supply can be reduced to a small fraction of what the plant will use, because such crops can draw their main supply of nitrogen from the air.

The amount of soluble phosphoric acid is ordinarily increased above what plant analysis calls for, because the solubility is more or less decreased after the fertilizer comes in contact with the soil.

The proportion of sulphuric acid used in making a superphosphate is generally as great as possible without impairing the dryness of the finished manure. It is usually more than sufficient for the realization of the equation given above. It is now supposed that the reaction which occurs takes place in two stages, the sulphuric acid first liberating an equivalent of phosphoric acid, which then reacts with the remaining $\text{Ca}_3(\text{PO}_4)_2$. The presence of calcium sulphate tends to solidify the mass

by combining with 2 molecules of H_2O and setting like plaster of Paris.

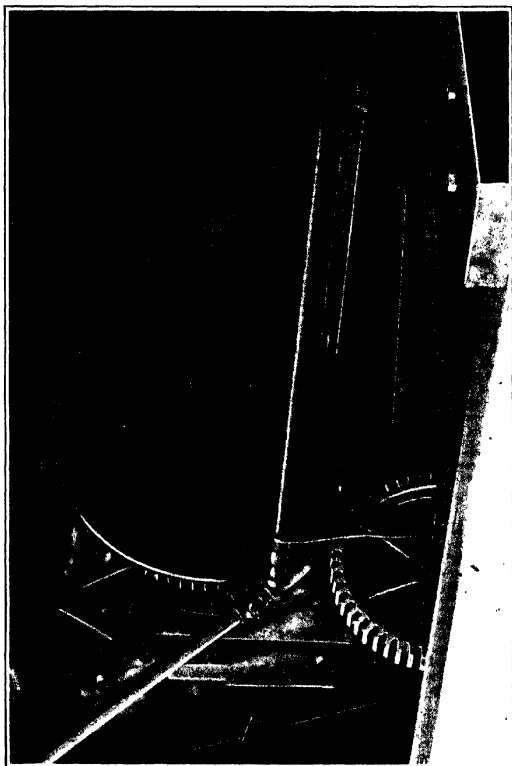
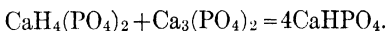


FIG. 4 —“Rinser” and its Gearings.

The value of a superphosphate depends on its content of phosphoric acid soluble in water, which

is commercially called "soluble phosphate"—i.e., the amount of phosphoric acid found, on analysis, to be soluble, is calculated back to $\text{Ca}_3(\text{PO}_4)_2$. An ordinary superphosphate will contain 24 to 30 per cent of soluble phosphate, 40 to 45 per cent calcium sulphate, and 2 to 3 per cent of insoluble phosphate. Attempts have been made to produce superphosphate containing more soluble phosphoric acid than the quantity mentioned above, in order to save carriage; thus "double superphosphate" is made by extracting an ordinary superphosphate with water, removing the calcium sulphate by means of a filter press, and evaporating the liquor with phosphate that has already been treated with a quality easily attacked by phosphoric acid. Such preparations may contain 80 to 90 per cent of soluble phosphate.

When superphosphate is kept, a portion of the soluble phosphate becomes insoluble in water owing, it is supposed, to the interaction of calcium superphosphate $\text{CaH}_4(\text{PO}_4)_2$, and normal calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, thus:



A further reaction, which has been already mentioned, occurs between the ferric oxide and alumina contained in crude phosphate and a portion of the phosphoric acid, insoluble ferric phosphate (FePO_4) and aluminium phosphate (AlPO_4) being formed. Although such "reverted phosphate" is insoluble in water, it is more soluble in saline solu-

tions—e.g., ammonium citrate solution—than is the natural phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and is reckoned as possessing a certain manurial value. These points have to be taken into consideration in the analytical examination of superphosphate.

When a mineral phosphate will not pay for conversion into superphosphate it may be used for the production of precipitated phosphate, which consists mainly of "dicalcium phosphate," CaHPO_4 . The preparation is conducted by dissolving the phosphate in hydrochloric acid, sufficiently diluted to leave siliceous matter and much of the oxides of iron and aluminium undissolved. The solution is neutralized by lime or chalk, when the precipitated phosphate is thrown down. It has been proposed to utilize waste calcium sulphide for this precipitation, the point of neutrality being discernible by the formation of FeS ; the H_2S evolved is collected for use as a source of sulphur. As already stated, this form of calcium phosphate is more valuable than $\text{Ca}_3(\text{PO}_4)_2$, and, being precipitated, is very finely divided; it contains up to 40 per cent of P_2O_5 , and is much used abroad.

CHAPTER VIII

MANUFACTURE OF SUPERPHOSPHATE

THE manufacture of superphosphate comprises three principal operations: 1. Grinding the raw material. 2. Rendering the ground raw phosphate soluble by sulphuric acid. 3. The drying of the superphosphate.

Raw phosphate should be carefully ground, because it is found that the fineness of the phosphate contributes to a great extent to a perfectly successful superphosphate. Thus the powder should not leave more than 10 per cent of residue on a 70 mesh sieve, and this residue should not exceed the size of groats; it is only at this cost that all the phosphoric acid is rendered soluble. Certain phosphates are delivered ground, others in lumps of the size of the fist. To lend itself well to grinding the phosphate should be dry. Florida phosphate especially should not contain more than 1 per cent of moisture, while Algerian phosphate grinds very well with 5 per cent of water. When dealing with phosphate drenched with sea water in transit or accidentally in the warehouse it is extended on a drying platform of sheet iron heated by the combustion gases or over flues from the boiler furnaces. For the grinding of phosphate at

the présent day ball mills—continuously fed and discharged—are in general use, which owing to their strong construction and stable working answer well for the purpose. In older factories flatstone mills are frequently used. Griffing crusher with a walking beam has likewise some rare partisans, but it is costly and requires repairs which become heavy in the end. The material to be introduced into this grinding machine ought preferably to be reduced, and for that purpose edge runners are suitable. The crusher, with blades—disintegrator—is likewise used, but only to crush phosphate in large pieces or rock phosphate. These machines will now be considered.

Edge runners consist generally of two stones turning on a circular plate round a vertical shaft; at the same time each stone turns round its own horizontal axis, and grinds the material both by crushing and rubbing. The horizontal axes of the two mills are independent of one another and each connected with the vertical shaft by means of a hinged crank. The stones can thus be raised or lowered independently of each other. The material is fed into the mill directly, by shovel or by an elevator; it is drawn continually under the stones by collectors, and when it is sufficiently ground, it is evacuated by the automatic discharge, sifted and bagged up. Two men are sufficient to attend to such a mill.

Flatstone mills are built either with the upper stone stationary or the lower stone stationary, ac-

ording as it is the upper or lower stone that is made to revolve. Mills of the first kind are used for crushing very hard phosphate, those of the second kind for soft phosphates. The foundation consists of cast-iron columns or a hollow cast-iron support, on which the cage of the mill is fitted up. The shaft of the mill is sustained by a movable bearing with collar; its lower part rests in a socket. The bearing with collar is screwed to the bottom of the mill cage and completely protected from dust. The adjustment of the revolving millstone is done by means of an endless screw or by lever transmission with screw, and hand fly-wheel. The number of revolutions is about 120 per minute for mills five feet in diameter, under which conditions a mill can grind about five tons of phosphate per hour with 20 horse power. The mill is fed by a cup elevator and shaking hopper; a single workman with an assistant can attend to two pairs of stones placed side by side. The mills of the same group are generally driven by a single main shaft by direct cog-wheel gearing. Generally three pairs of stones are in use, two of which are at work and the other pair being faced. A great many other kinds and classes of mills are used among which are the ball mills, Pfeiffer's Mill with combined air separator, which is a kind of ball mill, and the jaw-breaker mill.

The phosphate was formerly rendered soluble in pits where the sulphuric acid and phosphate were hand-mixed with suitable tools; in other

words, they wrought like masons making mortar. But for thirty years this work has been done exclusively by mechanical means, which enables the work to be done more rapidly and in larger quantities at a time.

Consequently the mixing pit has been enlarged so much that in its new form it constitutes the chamber, or more familiarly the "den" or "house" in which the phosphate is rendered soluble. This chamber is closed and care has to be taken to eliminate and render inoffensive the toxic gases which are disengaged from the material during its decomposition.

To mix the acid with the phosphate a "mixer" or mixing machine is used, constructed and installed thus: The mixer consists of an egg-shaped pan 64 inches wide at the top and 48 inches wide at the bottom, fitted with two discharge doors, with lever and counterpoise, which enables the mixing to be run into an enclosed space, called the decomposition chamber, which is built on the ground floor or sunk in the ground. In the pan a vertical shaft turns, driven by a cog-wheel gearing and carrying blades of a special form arranged in a helicoid manner; these lift, throw down, and triturate the mass, after the style of a plough as it works the ground, and prevent it at the same time from being deposited and attached to the sides. It suffices to pull the bent levers to open the discharge doors, and thus let the liquid fall into the decomposition chamber, "den" or "house."

The pan is made of cast iron, with 2 per cent of a special alloy which renders it very resistant to acid. The arms of the agitator and the blades as well as the valves are of cast steel. The mixing shaft makes sixty turns a minute; the mixing is triturated until the pulverized phosphate is fine enough to pass through a 70-mesh sieve. As the mixture remains longer in the liquid state, the length of time occupied in mixing must be prolonged. The acid, contained in a lead-lined tank, is drawn into a measuring tank by turning a valve; it then flows through a 2-inch lead pipe into the mixer in the form of a fine spray. At the same time the crushed phosphate—previously weighed and laid on sacks on two inclined planes to right and to left of the mixer—is run into the mixer. In certain factories the phosphate is brought to the mixer by an elevator, and received in buckets by means of which it is run into the mixer. The bags retain about 1 per cent of phosphate in the fabric. The mixer can take a charge of about 495 to 550 pounds. When the phosphate is rich in carbonate of lime the mixture froths and threatens to prime. Such a mishap is obviated by diminishing the amount of phosphate. The acid and phosphate ought to be run in simultaneously and never after each other. The mixer works continuously with no stop except in case of a breakdown. When one mixing is finished the sides of the mixer are rapidly dusted with a little phosphate to neutralize any free acid left there which might corrode the metal.

The working of the mixer requires three men; the first takes charge of the machine, the second su-

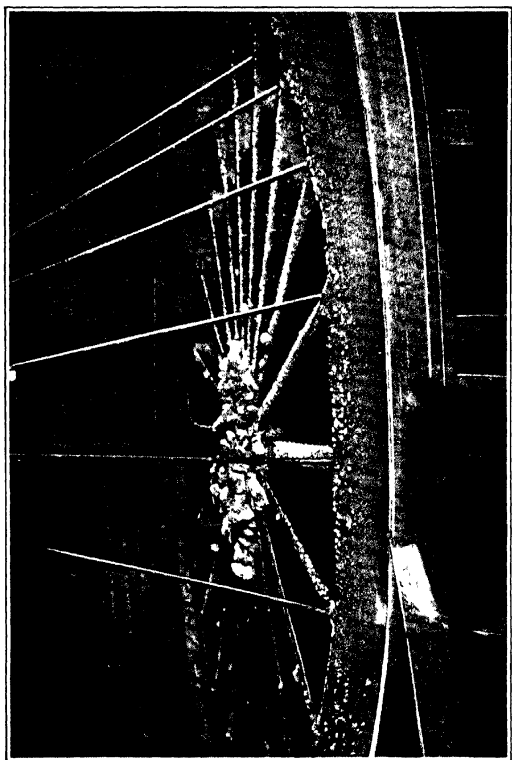


FIG. 5.—Picking Table Showing Phosphate Ore on Table.

perintends the measuring and running in of the acid, the third brings the sacks of phosphate.

The charging of the mixer lasts about two minutes; agitation takes two minutes, according to the nature of the phosphate; discharge takes half a minute. The "den" may be filled to three-fourths its height; the vacant space serves as a regulator for the evacuation of the gas. The decomposition of the phosphate by acid is effected not in the mixer, but principally in the "den" or "house." Cold acid is used, that is, acid the temperature of which varies between 25 degrees and 30 degrees C. and of a density between 50 degrees and 55 degrees B \acute{c} . When the acid is at a lower temperature the mixing does not heat enough to drive the water off, and yield a dry superphosphate. When the acid is too hot the mixing thickens too much in the mixer, in which case the acid may be further diluted.

Owing to the gas given off, the thick liquid effervesces, and forms air-bells which rise to the surface; at the same time it heats up to 248 to 302 degrees F. Gradually it settles in the "den" and after an hour it sets. An addition of dolomite (carbonate of lime plus carbonate of magnesia) keeps it liquid for some time longer, so that the water evaporated is then much greater.

All the heat given off by the reaction ought to be utilized with that end in view, that is, carrying off the water. It is only when this is done that perfect solution is realized, and that a superphosphate that will behave well on subsequent manipulations is obtained. Of recent years attempts

have been made to use hot sulphuric acid and inject hot air into the chamber, so as to render the phosphate perfectly soluble and to start the drying of the superphosphate, so as to simplify the final operations. But the results obtained were not satisfactory. The opinion of certain specialists may be endorsed. Such experiments will never be successful, because it is irrational to exceed a temperature of 100 degrees C. in the "den" except in the case of phosphate of a very good quality of which there is no need to fear retrogradation. It is better to leave the substance to itself during its chemical transformation and let it be settled by insensible gradations. Experiments show, moreover, that the injection of hot air into the mass gives it the consistency of mastic, which the manure manufacturer always tries to avoid, knowing full well that the porosity of the superphosphate is the best condition to realize for subsequent operations. The construction of the decomposition house is not very complicated. The walls are two-brick thick; they are covered inside with a coating which resists acid. To consolidate them and prevent them yielding under the pressure of the mixing they are fortified by iron T pieces, fixed to the base by masonry, and joined to the roof by cramping irons. The roof consists of iron T pieces three feet apart, laid on the walls and connected together by iron rods or arches of masonry, the whole being covered by a coat of cement. All the ironwork is covered by paint to resist acid fumes. The house

is fitted with solid oak or pitch pine door consolidated inside by planks placed crosswise in the gutters. The chinks of the planks and the doors are luted with a paste of clay so as to prevent air penetrating.

In the early days of manure manufacture only one "house" was used, and the mixer was installed in the center of the ceiling of the house; then two houses were installed with the mixer stride-legs between them; finally, later on, four houses have been built and the mixer placed at the crossing of the party walls. This plan gives excellent results. The mixer in that case is fitted with four discharge doors each of which empties into a house of its own. Each "den" has a capacity of 50 to 100 tons according to the size of the factory.

Attempts have been made to find methods of rendering phosphate soluble more rapidly and more completely than by the processes actually used. To accomplish this the phosphate is reduced to a very fine state to pass through a No. 100 sieve. A paste is made of it by drenching it with water or with acid of 10 to 20 degrees Bé. and finally adding the rest of the acid at 60 degrees Bé. But this process was soon abandoned, for the action was too violent and the metal of the mixer was attacked by the acid.

Attempts have been made to render phosphate soluble by mixtures of hydrochloric and sulphuric acid without any great advantage. The superphosphate contained 30 per cent of hydrochloric

acid, which rotted the bags, besides the mixture of sulphuric acid and hydrochloric acid attacks the metal.

The gases formed in the superphosphate "dens" cannot be allowed to escape into the atmosphere without being purified, in consequence of their bad smell and corrosive action. They are generally passed through a wash tower by means of a fan. The fans should be rather powerful, so that the amount of air drawn into the "den" during discharge is sufficient to allow the laborers to empty the "den" under good conditions.

CHAPTER IX

COMPOUND MANURES

THE manures generally used for admixture with superphosphates are Peruvian guano, bone dust, sulphate of ammonia and nitrate of soda, but the Peruvian guano now shipped from places of production is much less rich in nitrogen than that imported in the past. Its place is taken by sulphate of ammonia, ground horn, dried blood, dried meat, etc. Superphosphate of potash is also prepared. The mixing is done as much as possible after the phosphate is dissolved. Mixing is not done in the dry state, except when it cannot be done otherwise.

Hand labor is the best for this kind of work. The materials, previously weighed and sifted, are made into a two-ton heap by means of a portable box or barrow capable of holding two cwt. To turn the matter properly the shovel is plunged into it vertically, so as to mix it, then after having sifted it, it is made into a heap in the inverse order, that is to say, by lifting it from the ground to throw on to the middle of the heap.

These manipulations are sometimes rather unpleasant, on account of the disengagement of dust, etc., nevertheless they form the best method of mixing. The materials so mixed are afterwards

passed through a disintegrator or through a toothed crusher and a very homogeneous mixture is thus obtained. Inert materials should be avoided in these mixings. By mixing high strength superphosphate with low strength superphosphate common kinds can be made without recourse to inert materials, such as sand, plaster, etc.

Although the composition of ammoniated superphosphate is very variable, the most usual strength being 9×9 , 5×10 or 6×12 , the first figure indicating the percentage of nitrogen, the second the percentage of soluble phosphoric acid, this manure is in great esteem. It is analogous to dissolved Peruvian guano to which farmers are accustomed. It, moreover, presents this advantage, that its acid retrogrades less easily in the soil than that of pure superphosphate, seeing that the sulphuric acid combines first with the bases which it encounters in arable land. The mixture of superphosphate with sulphate of ammonia is easily made. Sulphate of ammonia is delivered in a finely ground granular condition. It contains 24.5 per cent NH_3 = 20.2 per cent N and about 1 per cent moisture, which is an advantage for the manufacture, for the mixture 9×9 must be delivered with a maximum of 6 to 7 per cent of moisture, that of 5×10 with a maximum of 8 to 9 per cent moisture, if it is desired to avoid annoyances by the formation of lumps or loose caking in the sacks. To obtain very homogeneous superphosphate of ammonia, the sulphate of ammo-

nia is added during the "dissolving" of the superphosphate by dissolving this salt in the sulphuric acid used to decompose the superphosphate, but this method of proceeding is not applicable except with small amounts of sulphate of ammonia.

The process generally used in making superphosphate of ammonia is as follows: The dry superphosphate of ammonia delivered in 10-ton wagons, being stored and analyzed, the amount of superphosphate and sulphate required to give a mixture of 9×9 has been calculated. Suppose that the sulphate of ammonia contains 20.5 per cent N, then 20.5 kg. correspond to 100 kg. $(\text{NH}_4)_2\text{SO}_4$, 9 kg. correspond therefore to

$$\frac{100 \times 9}{20.5} = 42 \text{ kg. } (\text{NH}_4)_2\text{SO}_4.$$

There remains then for the superphosphate $100 - 42 = 58$ kg. These 58 kg. of superphosphate must contain 9 kg. of soluble phosphoric acid, which corresponds to $\frac{100 \times 9}{58} = 15.5$ per cent phosphoric

acid. To make the mixture the 10 tons of sulphate of ammonia are laid in a heap 33 feet long and on each heap the necessary portion of superphosphate to the total 12.77 tons. Two laborers mix the two with the shovel, making the whole into one heap and recommence the same in an inverse direction. The mixer is then passed through a disintegrator or toothed crusher, then it is laid on a

big heap in the warehouse for the ingredients to combine.

Mixtures of superphosphate and sulphate of ammonia exhibit phenomena of a peculiar nature. They gradually heat and become damp to the touch; they dry again, and owing to the formation of gypsum, they harden more and more. The reaction lasts for a variable time. It depends on the nature of the superphosphate, and its manner of manufacture, and may end in fifteen days, when the mass is in a large heap and exposed to a certain pressure. Superphosphate of ammonia forms a hard rocky mass, the shifting of which is expensive, for one is obliged to blow it up with gunpowder. However, only neglect of the man in charge of the mixer in not running in the proper amount of acid would produce this. It is then crushed by a disintegrator, is passed through the sieve, and bagged up immediately afterwards, for it does not solidify again if made according to rules, that is to say, if each grain of sulphate of ammonia is united to its grain of superphosphate to form a sulphophosphate. To diminish the hardening as much as possible, sand or better still powdered peat, sawdust, wool dust or chimney soot are added, and in the second place, immediate saturation of the sulphate of lime by the addition of a little water. The second grinding is therefore necessary to effect the perfect mixing of the two ingredients. In fact, if the substance be analyzed after the first crushing, there will be found 8.8



FIG. 6.—Drying Shed, Showing Piles of Phosphate Ore Piled up on Ricks of Wood Ready to be Fired for Drying out Water.

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per cent of phosphoric acid and 9.2 per cent of nitrogen, together 18 per cent, but after the second crushing the product uniformly shows 9 per cent of phosphoric acid and 9 per cent of nitrogen. This method of preparation serves, equally, for all the mixing if desired to make superphosphate of ammonia 5×10 . For 100 kg. of mixture, take $\frac{100 \times 5}{20.5} = 24.4$ kg. of sulphate of ammonia of 20.5 per cent N, and consequently 75.6 kg. of superphosphate containing $\frac{100 \times 10}{75.6} = 13.2$ per cent phosphoric acid. If it be a case of a wagon of 10 tons of sulphate of ammonia, 41 tons of the mixture will be obtained of the 5×10 mixture, requiring consequently 31 tons of superphosphate. It is easy to bring the superphosphate to the right strength by mixing it with a high, grade superphosphate, or with gypsum free from iron, alumina, and carbonate of lime. The low, grade superphosphate and gypsum act in the nature of a "filler."

In regard to the manufacture of superphosphate of ammonia and potash, this is prepared in the same way. Suppose it is desired to prepare a mixture of this nature with 5 per cent of nitrogen, 7.5 per cent of potash, and 9 per cent of phosphoric acid, and that there was to be used for the purpose sulphate of ammonia with 20.5 per cent N, and potash salts with 37 per cent K. To get 100 kg. of superphosphate of ammonia and potash it is therefore

necessary to use $\frac{100 \times 5}{20.5} = 24.4$ kg. sulphate of am-

monia. $\frac{100 \times 7.5}{37.0} = 20.3$ kg. of potash salt and con-

sequently 55.3 kg. of superphosphate testing

$\frac{100 \times 9}{55.3} = 16.27$ per cent of phosphoric acid. Ten

tons of the sulphate of ammonia used would therefore give 41 tons of the compound manure. It would thus be necessary to use 31 tons of potash salts plus superphosphate, say 8.32 tons of the first, and 22.68 of the second. These manure mixtures find an outlet chiefly in regions where the vine, tobacco, the hop, and vegetables for preserves are cultivated. They are likewise esteemed for the culture of the sugar beet, barley, and potatoes. Mixtures of superphosphate and potash salts become readily moist in the store, so that they cannot be prepared a long time in advance. The use of calcined salts prepared from the waste of potash factories, have the drawback that they generally contain magnesium chloride. When they are dried with precaution at 100° C. they are free from basic magnesium compounds. The retrogradation of the soluble phosphoric acid in mixed manures under the action of the basic salts of potash have been studied. By treating salts of potash in the reverberatory furnace to partial fusion, at about 800° C., the magnesium chloride which they contain is decomposed by its water of crystallization. A molecule of magnesia

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can retrograde a molecule of phosphoric acid, from which it follows that one part of MgO can render 3.55 per cent of phosphoric acid insoluble. If one uses, for example, twenty-nine parts of potash with 2.05 per cent of free magnesia, percentage controlled by estimation, the $\frac{2 \times 0.5 \times 29}{100} = 0.59$

parts MgO suffices to combine $0.59 \times 3.55 = 2$ parts of phosphoric acid; as an actual fact, only 1.4 of insoluble was obtained, which proves that the magnesia did not exert all its action. The cause lies in the slight solubility of magnesia, and in the fact that the salts of potash combine partially with the precipitate formed, so that a part of the phosphoric acid of this latter remains in solution.

The use of nitrate of soda in compound manures is rather restricted; it is used in making nitrophosphate, sometimes in nitrophosphate of ammonia. It is found that nitrate of soda and sulphate of ammonia are incompatible, and that in fact it is better to use these manures separately. Besides, mixtures of superphosphate and nitrate sometimes enter into spontaneous combustion in the bags. This is caused by the superphosphate fresh from the mixing "den" being mixed with the nitrate and bagged up before it has had time to cool. Cold superphosphate, however damp, does not act on nitrate of soda, unless in very warm weather. They are no longer objects of terror to the manufac-

turer, providing that the superphosphate used has been properly made and the dry nitrate of high percentage mixed with a superphosphate, likewise dry, does not give off nitric acid and cause a loss of nitrogen, as was often the case formerly when superphosphate were wet and the nitrates charged with chloride of sodium. The sodium chloride decomposed by the free phosphoric acid caused the bags to burst in transit, for there is no substance which rots bags like free chlorine and fluorine, two elements given off when nitrate and damp superphosphate are mixed.

Finally, a manure is made for meadows by mixing kainit with superphosphate or with basic slag. The mixing entails no difficulty. The ingredients are mixed with a shovel, then the heap is turned over, the product perhaps passed immediately to the centrifugal crusher, then to the sifting machine. If the kainit be in blocks or lumps it must be passed to the crusher to reduce it to the desired fineness.

It has already been remarked that in the case of the superphosphates of ammonia of high strength, the phosphoric acid soluble in water did not retrograde even when the superphosphate entering into the mixture was of such a nature as to readily lend itself to retrogradation. The cause of this phenomenon is of both a physical and chemical nature. The more the superphosphate is distended by ballast, which is here sulphate of ammonia, the more distant

the particles are from one another which preserves their condition. From a chemical point of view, sulphate of ammonia possesses the property of hindering the basic sesquioxides from precipitating themselves, but it is clear that a retrograded superphosphate cannot be improved by mixture with sulphate of ammonia.

CHAPTER X

NITROGENOUS MANURES

THE most, widely distributed nitrogenous manures are nitrate of soda and sulphate of ammonia. A third class of purely nitrogenous manures is that represented by animal waste. These latter products are of considerable agricultural importance, although the manure trade does not seem to take them sufficiently into account. These three forms of nitrogenized manures are not only differentiated by their chemical composition, but by their mode of action in the soil. They form, therefore, three distinct classes, which will be examined.

Nitric acid compounds have been known for a long period. It is probable, according to Herpath, that the ancient Egyptians used nitrate of silver to make their inscriptions on the bands in which they wrapped their dead; it is the same chemical compound as that known as infernal stone, which is used to mark linen and the skin. As far back as the eighth century of the Christian era, Geber and Marcus described a body which they called *salpetrae*, which corresponds with saltpetre, or nitrate of soda. In the twelfth

century, Raymond Lulle called this body sal-nitri. Since then the term saltpetre has been used to designate nitrate of potash, while nitrate of soda is called Chili saltpetre, or nitre.

Nitric acid consists of nitrogen, oxygen, and hydrogen; its chemical formula is HNO_3 . It thus contains fourteen parts of nitrogen (22.2 per cent), forty-eight parts of oxygen (76.19 per cent), and one part of hydrogen (1.59 per cent.) It forms a very caustic fuming liquid. In the concentrated state it has a density of 1.52, but the commercial acid is generally much weaker. It decomposes easily. It gives up a portion of its oxygen to oxidizable bodies, such as carbon, sulphur, sulphurous acid, and then passes to less highly oxidized states. Metallic zinc reduces dilute nitric acid, and converts it into nitrate of ammonia. With bases it forms salts, which with the exception of some basic metallic salts, are soluble in water. Nitric acid is formed almost exclusively by the oxidation of ammonia, or of nitrogenous matter of animal origin, under the action of the air in presence of bases such as the carbonate of lime. However, this spontaneous formation in the soil is very slow. It is, on the other hand, very rapid in Southern countries, where the conditions of temperature and of moisture in the air conduce considerably to the oxidation of nitrogenous animal matter.

South American nitrate of soda is distinguished, more especially from ordinary saltpetre, by the

fact that its acid is combined with another alkali. In Indian saltpetre it is combined with potash, while in Chili saltpetre it is combined with soda. It is met with in the Pampas of Peru, of Chili and Bolivia, between 19 and 27 degrees of south latitude; it abounds especially in the province of Tarapaca (formerly Peruvian, now Chilian), and in the desert of Atacama. The nitrous mineral caliche or terra saltrosa, occurs as a layer 1 to 6 in. thick under a bed of conglomerate, consisting of sand, feldspar and pebbles, amalgamated by a cement consisting of clay and different salts forming a bed 20 to 30 in. thick. Its color varies from gray to brown. The conglomerate bed is sometimes wanting, so that the mineral crops out at the surface.

The caliche is never pure nitrate of soda. It contains mixtures of nitrate of potash, common salt, iodide and bromide of sodium, alkaline sulphates and sulphate of lime mixed with sand. It only contains on an average 25 per cent of nitrate. Picked pieces contain more.

Opinions differ as to the method of formation of this deposit which occupies a surface of about 150,000 acres and contains about 170,000,000 tons. It is believed that the nitrate is formed from the nitrogen of guano deposits, which covered the shores of a great soda water lake by a process analogous to that to be seen in Hungary in our own time. The soda salts of the sea water would simply convert the saltpetre

into nitrate of soda. This opinion has in its favor all the facts and circumstances met with



FIG. 7.—Sample of Phosphate Ore from a Laminated Boulder.

in the deposit. Moreover, traces of guano are still found in the crude salts. To extract the

crude salt a hole is dug in the ground 20 in. in diameter; when the saltpetre bed is reached a chamber 35 to 40 in. in diameter by 12 in. deep is excavated and 3 to 4 cwt. of powder inserted. By exploding the powder by means of a fuse, a considerable surface of the deposit is laid bare often on a radius of 40 ft. from the hole. The crude salt is hand picked, to eliminate stones and fragments of less value; it is charged into baskets or into trucks, which camels transport or draw to the melting workshop. To dissolve the crude caliche three kinds of apparatus are used:

1—Open Cast-Iron Pans—Paradas.—These are heated by naked fires. Two pans 6 ft. 6 in. in diameter are used for one furnace. Well water or water from a ~~previous~~ previous operation is run in, then it is charged with caliche or crude saltpetre reduced to pieces the size of the fist. When the solution is concentrated enough, it is run into cases or boxes, where it clarifies; it is then decanted on the top of the depot and run into iron or wooden crystallizers; 40 per cent of crystals is thus obtained and 60 per cent of mother liquor.

2—Cylindrical Vertical Pans—Marquinas.—These are heated by direct injection of steam. They are 26 to 33 ft. with a diameter 13 to 16 ft. Each of these pans yields in 24 hours, 45 to 148 tons of saltpetre. The clarified solution is poured into wrought iron crystallizers 13 to 16 ft. square and 20 in. deep; crystallization requires

three to four days. The steam given off contains an important amount of iodine which can be avoided by an addition of soda.

3—Vessels Heated by a Closed Tubular Bundle or Steam Coil.—This method has been introduced by British and German companies. These vessels measure 36 ft. long, 6 ft. wide by 6 ft. high, into which the mother liquor and the wash water are run and heated to boiling. Then six trucks of perforated wrought iron containing about four tons of caliche are run in. The nitrate dissolves in the water while the residue remains in the trucks. To hasten solution the liquid is agitated by injection of steam and of hot air under the truck by means of a Koerting's injector. This plan works more economically than the preceding one. At the same time the solutions so obtained are purer and more concentrated. To get a ton of nitrate requires three tons of caliche. The crystallized nitrate is left to drain, then it is dried in the open air. Nevertheless it always remains slightly moist owing to the presence of chlorides of calcium, of magnesium, and possibly also of nitrates of calcium and magnesium. It crystallizes in rhombohedra, and has a dirty reddish gray appearance, due to its oxide of iron content and to bituminous substances. The residue left by the solution still contains from 15 to 35 per cent of NaNO_3 . It is boiled with water and a weak solution of 43° to 45° B. obtained, which is utilized to dissolve a fresh

charge of crude salt. The muds from the clarification are treated in the same way.

Nitrate of soda is marketed in the original sacks weighing 254 to 308 lb. It forms a mixture of crystals of different sizes. It draws moisture from the air and when it is preserved in sacks they rot after some time and tear with the slightest pull. When the sacks are emptied, one part of the material, always moist, remains adherent to the fabric, from which there results not only a loss of matter, but also a loss of sacks, as these gunny bags then become unutilizable.

Nitrate of soda is often colored yellow by the presence of chromate of potash or violet by the presence of nitrate of manganese. The presence of nitrate of potash or magnesium chloride renders it deliquescent, hence arises loss by the drainage of dissolved nitrate; that is why the bags are lodged on beds of plaster or clay which absorb the liquid. But it is best to spread the nitrate intended for mixing in a not too warm place. The bags are washed with tepid water, and the solution is added in the manufacture of superphosphate which has to be mixed with nitrate, or it is concentrated in a pan. Certain manufacturers content themselves with beating the bags free from the adherent salt. If the nitrate ought to be employed alone it is screened and the lumps crushed in a disintegrator, or in the toothed roll crusher. It is dried in the old phosphate drier. However, if it be stored for a certain time

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in a place that is not heated, it gradually becomes moist. In consequence of the risk of fire, the building in which nitrate is stored should be isolated and built entirely of iron.

CHAPTER XI

THE FIXATION OF ATMOSPHERIC NITROGEN, MANUFACTURE OF CYANAMIDE AND NITRATE OF LIME. EXPERIMENTS WITH CYANAMIDE

ATMOSPHERIC air is an inexhaustible source of nitrogen. It is calculated that the column of air which covers two and a half acres of ground contains 79,000 metric tons which gives or is equal to 20,000 tons of nitrate of soda per acre. But nitrogen exists in the free state in the air, and to render it assimilable by plants, it is necessary to convert it into appropriate compounds. We know that this conversion can be effected by certain bacteria of the soil, such as leguminous bacteria, etc., likewise by certain phenomena which occur in nature, such as electrical discharges; especially lightning. But the amount of nitrogen brought into the soil in this way is far from being sufficient to cover the requirements of plants, and vigorous efforts are now being made to capture atmospheric nitrogen under an assimilable form. Experiments made enable us to affirm that this is possible. But all the tentatives made in this direction show that the industrial fixing of atmospheric nitrogen requires the use of great

quantities of electrical energy. There are at present two chief methods of manufacture: (1) the Frank and Caro process, (2) the Birkeland and Eyde process. The first consists in combining atmospheric nitrogen dry and deprived of its oxygen, with calcium carbide, obtained by fusion in the electrical furnace of equal amounts of coal and lime. The product so obtained is termed nitrogen or cyanamide of calcium. The second process consists in oxidizing atmospheric nitrogen by electrical means, and converting it into nitric acid, which is put into commerce as nitrate of lime with 13 per cent of nitrogen, which has the greater analogy with nitrate of soda and which, like the latter, is assimilable by plants. The two products come on the market as more or less dark, dirty-gray powders.

As just mentioned, this process for the manufacture of nitrate of lime consists in oxidizing atmospheric nitrogen by electrical means. In 1903 Prof. Birkeland of Christiania observed that the electrical discharges from the alternate current, at an average tension, dispersed in the magnetic field, brought about the combustion of the nitrogen in the air. This process had the advantage over similar ones of requiring a much lower electric tension, say 5,000 volts in place of 15,000, and to furnish much higher yields of nitric acid. The air is burnt in an electrical oven having the form of a drum. This furnace was modified and improved by

Samuel Eyde. In this drum the air is submitted to a temperature of $3,000^{\circ}$ C. By rapid cooling the nitrous oxide (NO) formed in the electric flame is retained almost entirely, while in former processes it was in great part lost. The nitrous oxide issuing from the furnace at a temperature of 600° to 700° C. combines with the oxygen to form NO_2 , which is passed through a series of towers. It finally yields nitric acid of 50 per cent strength, which is saturated with lime. The mass is heated to 450° C., which is its melting point, then poured into cast-iron cylinders, where it solidifies slowly. In the beginning, crystallized nitrate of lime was manufactured and was difficult to use owing to its hygroscopic properties. This product melted between the fingers and thus could only be used mixed with peat dust. That was why manufacturers afterwards set themselves to make basic nitrate of lime; but this product contains only 11.7 per cent of nitrogen, which rendered its freight charges heavy, and formed an obstacle to its sale. Lately, the partially dehydrated salt tested 13 per cent of nitrogen. The first manufactory of any importance of this product was built at Notodden in Norway. The experience acquired in that factory has induced the management of the company to increase the plant, so as to make 8,000 to 10,000 tons per annum. This factory is maintained by the Badische Anilin und Sodafabrik. The unit of nitrogen

in nitrate of lime is sold at the same rate as the nitrogen in nitrate of soda.

Calcium cyanamide has of late years been the subject of numerous agricultural experiments. It must be observed in a general way that calcium cyanamide neither suits humic acid soils, peaty soils, nor light sandy soils. On the other hand, it may be used in all loamy soils of average fertility. Owing to the formation of dicyanamide, this manure ought to be spread at least eight days before sowing and covered in afterwards in not too superficial manner. The action of cyanamide is weaker than nitrate of soda; it is also slower than the latter. But as the unit nitrogen is supplied cheaper by the new manure, a greater amount can be used to restore the balance. Without doubt cyanamide deserves great attention. According to the experiments made, this manure succeeds very well on clay soils, but less so in sandy soils. It has been observed that the conversion of cyanamide into ammonia in the soil is effected by bacteria, for example, by the *B. Megatherium* and *Mycoid* and other species in part new. Nitrate of lime acts normally up to the second application in loamy soil and up to the third in sandy soil; but beyond that there is an injurious action, especially in loamy soils. The high percentage of basic nitrate of lime and the still higher percentage of nitrate of lime produce injurious effects.

Nitrate of soda, Chili saltpetre and sulphate of ammonia have regularly produced higher yields and better utilization of the nitrogen than cyanamide.

If the value of nitric nitrogen be expressed by 100, the value of the nitrogen in cyanamide is represented by 90. The lime nitrogen acts a little more feebly when it is decomposed in the soil, giving rise to the formation of dicyanamide resulting from the action of carbonic acid, humic acid, heat and the absence of bacteria. The factors which favor the action of cyanamide are uniform distribution, perfect mixing of the manure with the soil, sufficient moisture to the soil, and a loamy soil rich in bacteria, spreading at the latest on the 15th day of February for winter plants.

Cyanamide does not suit humic acid soils, where its action is uncertain and where it may poison plants. For the same reason its use is not recommended in light, sandy, somewhat torpid soils, especially those with an acid reaction. All other soils, especially loose friable soils, which contain enough lime and are regularly manured with farmyard dung, may be manured with cyanamide. The quantity to use per acre is 135 to 274 lb., according to the fertility of the soil.

As cyanamide gives off an enormous amount of dust which is possibly the most unpleasant defect of this manure, the best thing to do, if

a manure distributor be not available, is to mix it intimately with double its weight of not too moist soil and to spread it immediately. In no case should cyanamide be used as a top-dressing, at least until after the crop has been removed, for in that case it would be more injurious than useful.

Stored for a long time in casks, nitrate of lime suffers considerable loss in weight. Having been left in casks for five months it has been found to lose 20 to 25 lb. by volatilization.

CHAPTER XII

POTASSIC MANURES. MANUFACTURE FROM CRUDE SALT. MANUFACTURE FROM FELD- SPAR. MANUFACTURE FROM SUNFLOWER AND KELP PLANTS

* THE ash of plants consists for the most part of carbonate of potash, the caustic and detergent properties of which attracted attention from the very beginning of civilization. And as a matter of fact the ancients knew this substance and employed it in domestic economy as well as in industry. Aristotle described the manner of extracting potash from the ash of plants. His process is still in use in certain countries. It consists in submitting the ash to a series of washings with water, concentrating the lye by evaporation, and in calcining the residual selt. As plants leave only a small amount of ash, and as this does not wholly consist of carbonate of potash, it is clear that the yield of potash cannot be very great.

Carnallite forms the chief ingredient of crude potash salts. There are five crude salts known as Sylvinite—kainit, schoenite, polyhahite, krugite and carnallite.

In the manufacture of potassium chloride

(muriate of potash) the crude salt treated consists of a mixture of all the salts as mentioned on previous page. However, carnallite predominates; it forms 50 to 60 per cent of the crude salt, equal to a potassium chloride content of 13 to 17 per cent. The processes now used in the treatment of the crude salt in the manufacture of more pure potash salts (potassium chloride) are based essentially on the property of carnallite to decompose in presence of water into potassium chloride and magnesium chloride; it is therefore dissolved and potassium chloride separated from the solution by crystallization. The process is in itself very simple; what complicates it is the presence of quite a series of foreign salts accompanying the carnallite, the most important of which are rock salt (NaCl), in the proportion of 20 to 25 per cent, and kieserite, which forms 15 to 20 per cent of the crude salt. Other minerals, such as kainit, polyhalite, tachydrate, are rarely met with in large proportion; but they then are very troublesome in the process.

As the mines deliver the crude salt in big lumps, which were at first delivered ground, they must be crushed before treating. Formerly they were satisfied with crushing lumps by blows from a mallet with a long handle, but now all factories have installed mechanical crushers for the purpose; the machine most used is the jaw-breaker crusher already described.

The salt is then fed into a pan, in which it

is dissolved. The crushed salt falls from the mill into the receiver of a cup-elevator which delivers it directly into the dissolving pans or into a wrought-iron chute. The elevator is driven by a shaft on which is mounted the belt pulley. The dissolving pan is of riveted wrought-iron of a cylindrical form ending in a conical bottom. At the beginning of the cone is a perforated short bottom intended to retain the residues from the salt. These residues are run out through a manhole. The solution is drawn off by a tap. The pan is steam heated. In the early days the Stassfurt and Leopold factories wrought in an appreciably uniform style, but lately they have adopted different methods more conformable to the interests of each factory. The oldest method, still much employed, is the following: The dissolving pan is first partly charged with water, mother liquor, which is termed No. 2, with residual solution No. 1 and with clarified solution No. 3. After having brought this mixture to the boiling-point, by direct injection of steam, the crude salt is fed into the elevator, while continuing to boil without interruption. The carnallite soon dissolves and therefore the density of the solution increases gradually. The escaping steam by a suitable arrangement sets the liquid in motion and mixes its different components. When the density of the liquid reaches 32° to 33° Bé., the elevator is stopped, the steam turned off and the solution run

out. The residue remaining in the pan contains a large proportion of kieserite, common salt, and about 2 to 4 per cent of potash salts. In a great number of factories this residue is again taken up and boiled with a little water; the solution thus obtained consists therefore chiefly of common salt, a little magnesium chloride and magnesium sulphate. Its potassium content varies from 3 to 7 calculated as potash chloride; it is used solely to dissolve fresh quantities of crude salt. The proportions of the different solutions as well as the densities vary with the factory. The residues are thus more or less abundant and retain more or less salts. The best results are obtained by preparing solutions of 32° B \acute{e} . with lower densities; they retain a large amount of common salt; when on the contrary their density is higher they retain less common salt and more potassium chloride.

The crude solution as it comes from the pan is soiled with impurities; it is therefore run into clarification basins, where it remains for about forty-five minutes. These basins are rectangular, of riveted wrought iron, fitted with two apertures from one of which the clarified solution is run off, and from the other, the sludge. To prevent the clarified solution carrying the sludge with it, different arrangements have been made to retain it. After the clarified solution has been run off, it is led through a wrought-iron gutter

into underground crystallizers. As the solution cools in flowing through the gutters, it deposits a certain amount of salt containing 45 to 50 per cent of potassium chloride. This gutter salt is generally used in manure manufacture. It is generally treated with potassium chloride of a higher strength.

The crystallizers in which the solution cools and forms crystals of potassium chloride are of riveted wrought iron like the clarification basins; they vary in size and shape, sometimes deep because they occupy less space and yield larger crystal. When the solution is cold, which takes two to four days, the mother liquor No. 2 is decanted from the crystals of potassium chloride; it is run off by the gutters fixed under the crystallizers into wrought-iron basins or into masonry ones lined with cement. It is used either to dissolve the crude salt or treated directly as will be described further on. The potassium salt which is deposited in the crystallizers consists of a mixture of potassium chloride and common salt; it is still soiled by the adhering mother liquor. It crystallizes in the same form as sylvine, with this difference, that the crystals are not always perfectly formed; their size depends chiefly on the density of the solution of crude salt. When that has a density of 32° to 33° Bé. or still weaker density, crystals often 1 in. wide, of a pearly lustre, are obtained. When the solution is more dense, say about

33° to 35° Bc., it forms soft crystalline needles. It is clear that the size of these crystals must considerably affect the purity of the potassium chloride, as attenuated crystals must retain more mother liquor than large ones, and that consequently they contain more magnesium chloride. It may be remarked in passing that the salt that is deposited on the sides of the crystallizers is always more pure than that deposited at the bottom. To obtain high strength products, a portion of the two sorts may be taken, especially for continuing the treatment.

As potassium chloride of 60 to 70 per cent strength is hardly marketable, it is necessary to submit it to new treatment—that is, clarification. For this purpose it is run into vats, termed clarifying vats, fitted with a double bottom covered by cloth or with a network of osiers. It is covered with water, so that the water is 2 to 3 in. above the salt, and left in contact with it for five or six hours; then the clarified solution No. 3 is run off through a bung-hole in the bottom of the vat. This liquid runs into a special basin, from which it is run into the dissolving pans by a pump.

If the potassium chloride be not sufficiently enriched by a single clarification, this operation is repeated once or twice until the salt contains at least 80 per cent of dry potassium chloride. The above clarifying liquor constitutes a saturated solution. Now a solution of this

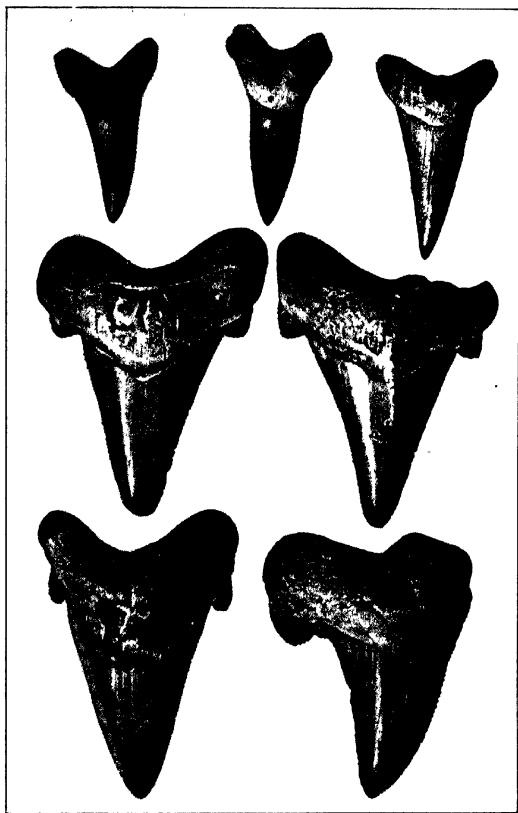


FIG. 8.—Shark's Teeth taken from the Hard-rock Phosphate-ore Deposits

nature contains at 15° C. 25 per cent KCl when it is prepared from pure potassium chloride, 27 per cent NaCl when it is made from common salt. If these figures be compared with those above, it will be seen that the magnesium chloride interferes with the solution of both the potassium chloride and the common salt. Now as the object of clarification is precisely to eliminate this latter, it follows that a potassium salt with low magnesium chloride content, consequently large-grained, will be more easy to purify in this way than a salt with high magnesium chloride content, fine-grained crystals. But clarification is a costly operation because its object is to redissolve a portion of the finished salt, therefore to work economically it must be done in such a way as to clarify as little as possible, that is to say, to produce large-grained crystals as far as possible. Starting from the salt an 80 per cent product would be obtained by a single clarification, while a fine-grain salt often requires two, sometimes three, clarifications to get a product of the same strength. It is clear that by this operation 95 per cent products and higher may be obtained.

The mother liquor not used for dissolving is concentrated by evaporation, for it still contains an important amount of potassium chloride. In the evaporation the greater part of the common salt separates out, because it is less soluble when hot than when cold, at the same

time as the double salt of potassium and magnesium, which is hardly soluble. This mixture of residual salts often contains 7.5 per cent of potassium, which corresponds to 12 per cent of potassium chloride, or 14 per cent of potassium sulphate. It is utilized by either extracting the common salt from it or by converting it into manure of low strength. In rational manufacture the residual salt should be washed in the pan itself; for this purpose the mother liquor No. 2 is used, as the salt as well as the pan itself is still very hot. When the evaporated solution is run off, the mother liquor with which the pan is drenched heats rapidly and dissolves the greater part of the potassium salt which is still contained therein. This solution is facilitated by stirring. When the density of the solution determined while boiling reaches 34° to 35° Bé., it is run through wrought-iron gutters into special crystallizers, where it deposits not potassium chloride, but a salt with tetrahedral crystals, the composition of which is analogous to carnallite. If the solution was sufficiently concentrated, the liquid which flows from the carnallite crystals (the final liquid) only contains 1 to 2 per cent of potassium chloride. In certain factories the bromine is extracted, in others the magnesia. The artificial carnallite thus obtained is dissolved in water in smaller pans than those used to dissolve the crude salt. The solution tested to 32° to 33° Bé. is run into vats,

where it deposits potassium chloride more pure than that got from the crude salt. The mother liquor of this salt is added to the first. As the carnallite from whence it comes contains less common salt than the crude salt, this mother liquor yields little residual salt. The salt yielded by artificial carnallite is clarified with very little water, and yields very high strength potassium chloride of about 95 to 98 per cent.

In most factories potassium chloride is dried in reverberatory furnaces. In recently erected factories the drying is conducted in cylindrical coil-heated tanks, in which an agitator with blades revolves, followed by a roller compressor. When the shaft revolves the blades turn up the salt, and the roller which follows makes them into a cake again, so that the surfaces are continually renewed. When the drying is finished the salt is run out through a chute and bagged up. In a general way factories which work according to the processes described above are content with producing 80 per cent potassium chloride; they rarely push the clarification so far as to make 97 to 98 per cent product, although the potassium chloride dissolved by the clarification can be recovered immediately in the crystallizers, while the mother liquor is used to dissolve the crude salt. To obtain 98 per cent salt without effort, the method of dissolving the raw salts is altered. The mother liquor, the small amount of clarifying liquor, and finally the

liquor used to boil the residual salt, are alone used as solvent; all addition of water is avoided. After having brought the solvent solution in the pan to the boil, the raw salt is run in as before and the whole boiled without interruption until the solution tests 35° to 36° B \acute{e} . At that density the carnallite in the crude salt easily dissolves if the liquid be hot enough, i.e., if the steam be of sufficient tension. Certain factories insert an agitator whose action contributes to mix the solution, consequently to obtain a better result from the crude salt. Nevertheless, the residue is sometimes rich in potassium chloride; and is boiled a second time with pure mother liquor. The solution so obtained is clarified in the same way as in the first method; on cooling, it deposits not potassium chloride but carnallite, which is allowed to drain and then dissolve in boiling water to extract the potassium chloride. As common salt, as well as kieserite, dissolves only slightly when hot in a concentrated solution of magnesium chloride, while potassium chloride is very soluble therein, it is clear that the solution prepared by this process should contain very little common salt, and also that the carnallite which crystallizes therefrom should contain very little, and the chloride of potassium furnished by the latter should be of high strength. This method, however, has the drawback of yielding a large amount of carnallite, the removal and solution of which require much labor

and steam and consequently fuel. This drawback is obviated by diluting the solution which flows from the clarification vats, with water, so that after complete cooling it yields chloride of potassium of high strength directly, and no longer carnallite. In this way the crystallization and solution of carnallite is conducted in a single operation. The advantages of this method of working are evident: Instead of treating as before, two different solutions and two different salts, only a single solution and a single salt have now to be treated. The potassium chloride so produced is so pure that when it is freed from magnesium chloride by a little water, it contains only 0.5 per cent of common salt, all the rest being potassium chloride with a little moisture and some slight impurities.

In the manufacture of potassium sulphate, the process is by drenching potassium chloride with sulphuric acid and calcining in a reverberatory furnace. The reaction which takes place is the same as that used to manufacture sodium sulphate from common salt and sulphuric acid. First of all the material heats, gaseous hydrochloric acid is given off, and acid potassium sulphate formed. Afterwards the temperature continuing to rise, the acid sulphate of potassium being weak acts on the remainder of the potassium chloride. A new disengagement of hydrochloric acid gas is produced, and finally potassium sulphate remains as a solid mass. As

the potassium sulphate as it comes from the furnace is in big lumps, it must be crushed before delivery to the farmer. In the same way as the price of potassium chloride is calculated on the basis of an 80 per cent salt, that of potassium sulphate is based on a 90 per cent salt, consequently 100 lb. of this product at 95 per cent equals 110 lb. at 90 per cent.

About 90 patents have been issued by the United States Government for extracting potash from silicate rocks. At least four may be considered modifications of the J. Lawrence Smith method, since the essential feature of each consists in heating the potash-bearing material with calcium carbonate and some metallic chloride.

The first of these, United States Patent No. 513,001, was issued to H. S. Blackmore in 1894. To produce a soluble potassium salt according to this patent, orthoclase, reduced to a fine powder, is mixed with finely powdered calcium chloride in about equal proportions to the potassium silicate present. To the mixture is then added an excess of calcium oxide and a sufficient quantity of water to render the entire mass moist. This is introduced into a sealed furnace, or retort and heated to a temperature of about 1100° C., whereby the water mixed with the mass is converted into superheated steam at high pressure, which is supposed to assist materially in the transformation of the orthoclase into

soluble potassium chloride and insoluble silicates of calcium and aluminium. The heating is continued for about two hours, and after cooling the mass is placed in vats and lixiviated.

The part of the process as patented which requires the moist mass to be heated in a sealed furnace to a temperature of 1100°C ., could obviously not be carried out on a large scale, for it would not be feasible to make a furnace which would stand the pressure produced at this temperature.

In 1900 United States Patent No. 641,406 was granted to G. J. Rhodin for obtaining soluble potassium from feldspar. In carrying out the process according to this invention, 1 part of feldspar is mixed with 1 part of lime and 0.2 part of sodium chloride, all in a finely powdered condition. The mixture is then heated in a closed vessel of iron or other material, or else in an open-hearth or blast furnace, to a bright yellow heat and maintained at that temperature for a considerable time, care being taken not to melt or fuse the mixture. The cooled mass which still remains in a powder may be applied directly as a manure, since the potash is claimed to be rendered available by the treatment, or it may be separated from the mass by treatment with acids.

In 1907 United States Patent No. 869,011 was issued to Ralph H. McKee for a process for obtaining potassium compounds from potash-

bearing material containing mica by essentially the same treatment as that covered by Rhodin's patent for the extraction of potash from feldspar.

United States Patent No. 987,436 was granted to A. S. Cushman in 1911 for a method for obtaining potash from silicate rocks. According to this method the feldspathic rock is reduced to as fine a subdivision as possible and mixed with finely powdered quicklime in the proportion of 100 parts of the rocks to 20 parts of lime. The mixture is then spread on a suitable conveyor, as belt or drum, in the form of a bed having a thickness from three-eighths to one-half inch. To the surface of this bed is applied a solution of calcium chloride in separate drops and of such a concentration that the amount of calcium chloride added should be sufficient to supply chlorine in quantities at least molecularly equivalent to the total alkali contained in that portion of the feldspar which becomes aggregated into lumps on the addition of solution. The aggregates which harden quickly at ordinary temperatures, are separated from the unconverted powder by screening, and then heated in a rotary kiln at a temperature preferable, but not necessarily, below the point at which a substantial part of the potassium chloride is sublimed. The product is discharged continuously from the furnace in lumps and may be crushed for use directly as a fertilizer; or the potassium chloride may be extracted by means

of water and recovered from the solution, or utilized there in any preferred way.

From a comparative study which was made of these patents it does not appear that the use of sodium chloride has any advantage over calcium chloride. The latter is a by-product obtained in large quantities in the manufacture of sodium carbonate, and is somewhat more effective than the former in bringing about complete decomposition of the feldspar, but when limited amounts of the reagents are used more potash is rendered soluble with the use of sodium chloride than with calcium chloride.

In these experiments the results show that while a considerable portion of the potash was rendered available when using approximately the proportions of the reagents stated in the patents the total potash in the feldspar was not rendered soluble in this way at the temperature specified. Thus, when 1 part of the feldspar is ignited with 1 part of calcium carbonate and 0.25 part of calcium chloride, which is 0.05 part in excess of that equivalent to the alkalis in the feldspar, only about 60 per cent of the potash in the feldspar is rendered soluble. Increasing the proportions of calcium carbonate and calcium chloride used produces a comparatively small increase in the amount of soluble potash obtained, and complete decomposition of the feldspar only takes place when one part is ignited, under the conditions of the experi-

ment, with about 1 part of calcium chloride and about 2 to 3 parts of lime. When this proportion of the reagents is used, considerable variation in the temperature of ignition will give the same results, and almost the entire amount of the potash is rendered soluble at a temperature below the melting-point of potassium chloride.

The results obtained on igniting feldspar with lime and sodium chloride are in agreement with those published by Rhodin, the author of the patent covering this process, who only claimed an extraction of about 14 per cent of the potash in the feldspar when using the proportion of the reagents stated in the patent. It was pointed out, however, that a more favorable result was obtained by using a larger amount of salt with a smaller amount of lime. Thus, when 100 parts of feldspar were ignited to 900° C. with 40 parts of salt, about 70 per cent of the potash in the feldspar became soluble, which agrees with the values given for approximately this proportion of the reagents.

Unless a large excess of calcium chloride is used, when ignited with feldspar and lime, no vitrification takes place on heating to a temperature up to 1050° C. The ignited mass remains in the form of a powder, and consequently the soluble material present can be readily leached out without the necessity of any previous grinding of the mass. The same statements

hold true when sodium chloride is used, but with a more limited variation in the proportion of the reagents which may be taken. Thus, a hardened mass is obtained when 1 part of feldspar is ignited to 1050° C., with 1 part of calcium carbonate and 0.25 part of sodium chloride, but if the proportion of calcium carbonate is doubled the mass remains in a powdered form. When calcium chloride is used, the mass does not harden on ignition, even with 1 part of calcium carbonate.

On account of its simplicity, the method of decomposing feldspar by heating with calcium carbonate and with calcium chloride (or sodium chloride) could undoubtedly be carried out on a large scale without involving any serious mechanical difficulty, and the method would thus be a practical one providing the value of the products obtained would compensate for the expense involved. Although pure feldspar may be obtained which contains upward of 15 per cent potash, the average grade of feldspar which could be mined on a large scale would undoubtedly contain less than 10 per cent. If potash be quoted at sixty-six cents a unit, then potash in a ton of feldspar containing even 10 per cent of this constituent would be worth only \$6.60 when converted into the soluble form. It is then evident that the value of the potash alone will not compensate for its extraction, or by any modification of it for which patents have been

granted; nor is it at all likely in view of the comparatively low percentage of potash in all silicate rocks that any process can be devised which will prove so simple that the value of the potash alone will pay for its extraction. So far as I am informed these processes have never been practical on account of the fact that in all of them the cost of producing the potash is greater than its market value. It may be that on account of the European War some of these processes will become commercially feasible. It seems safe to say, therefore, that any method to be economical must produce at the same time other products of value in addition to the potassium.

In a modification of the old Charles Bickell process, it has been shown that all the constituents of pure feldspar-lime clinker lie between the limits allowable in a good Portland cement, and that ferric oxide is the only necessary constituent absent. If commercial feldspar and lime were used, however, this would no doubt also be supplied in sufficient quantity, and at the same time the silica and lime would be reduced more closely to the mean of that found in good Portland cement, providing the feldspar does not contain an excessive amount of free silica.

In order that a clay may be suited for the manufacture of cement it should have a percentage ratio of silica to alumina of from 3 to 1 or 4 to 1. The ratio of these two constituents in feldspar is 3.5 to 1. In muscovite and leucite of theoretical

composition, the proportion of silica to alumina is less than 3 to 1, but in commercial samples of leucite-bearing rocks, the ratio is usually greater than 4 to 1.

A clinker of the same ultimate composition as that which results when feldspar and lime are heated together may also be obtained when part of the lime is replaced by sufficient calcium chloride to be equivalent to the potash and soda in the feldspar, the total calcium used remaining the same as before; in carrying out this experiment, the feldspar and lime were ignited to constant weight, and the calcium chloride thoroughly dried by heating in an air bath below its melting-point. Ten grams of the feldspar were well mixed with 2.0050 grams of calcium chloride and 15.7895 grams of calcium oxide, and the mixture then ignited in an open dish in the furnace at 1400° C. By this treatment the alkalies are volatilized as the chlorides. On igniting for one-half hour, the weight lost by the ignited mass amounted to 2.5632 grams, equal to 25.63 per cent of the feldspar. When expressed as the chlorides, the percentage of alkalies in the feldspar used, amounted to 25.82 per cent. It would appear, therefore, that practically the whole of the alkalies in the feldspar were volatilized during the first half hour of ignition. On continuing the ignition for one hour longer, the additional decrease in weight which took place, amounted to only 0.0090 gram. The residue was then analyzed for

potassium and chlorine, but only a small trace of each was found.

That shows that the volatilization of the potash in feldspar takes place more rapidly when part of the lime is replaced by calcium chloride than when feldspar is ignited with it alone, but in each case the ultimate composition of the residue obtained is the same. Any excess of calcium chloride used above that equivalent to the potassium in the feldspar is slowly decomposed at the temperature at which the ignitions were made, leaving behind the oxide of calcium.

Since the clay used in making cement contains in some cases as high as 3 or 4 per cent of potash, it might be expected that part would escape from the kiln and be collected with the flue dust (particularly in those plants where a process for collecting dust has been installed: This has been observed by several investigators to really take place), and the potash then collected is found to be in a soluble form. By the substitution of feldspar for clay in the manufacture of cement, the potash then collected would, no doubt, be greatly increased, but since the analyses of cement show the presence of alkalies, it follows that with the style of kilns now in use all the potash in feldspar could not be made available in this way, and that a larger proportion of the potassium would be volatilized by substituting for a part of the lime, sufficient calcium chloride to be equivalent to the potassium, is evident from the

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experiments already referred to, and experiments are now being taken on a large scale to compare the practicability of this procedure with the simple ignition of feldspar and lime alone.

According to census reports of 1910, the Portland cement manufacture in the United States during the year 1909, amounted to 65,000,000 barrels, or 13,000,000 tons, valued at approximately \$53,000,000. The maximum quantity of potash which it would be possible to obtain by the use of feldspar in the manufacture of this quantity of cement can be calculated if the potash content of the feldspar is known. This varies from about 16 per cent down to less than 8 per cent, but if 8 per cent be taken as the average percentage of potash in commercial feldspar, then 1 part of feldspar combined with 3 parts of calcium carbonate, equal to 1.68 parts of calcium oxide, would yield 0.08 part of potash and 2.6 parts of cement. Therefore, 13,000,000 tons of cement would produce 400,000 tons of potash. Again, quoting potash at 66 cents per unit, this would have a value of \$26,400,000, which is three times the value of the potash salts used in this country during the year referred to, and about twice the value of the imports for 1911. Whether or not this would cover the cost of the feldspar, its transportation, and the expense incident to the recovery of the potash, can only be determined by experimentation on a large scale; but the probability that potash salts can thus be

obtained in large quantities as a by-product makes this method of getting at the potash in feldspas quite promising.

In the manufacture of potash in the Caucasus from the sunflower plant, the ashes of the stem and the branches of the sunflower yield the raw material. The first potash factory was established in 1899 at Maikopp, by Schaponalow. Difficulties occurred at first because experience was wanting. But gradually the conditions of production improved, and new factories were started. According to the official statistics in 1907, 11 of these factories produced 475,563 poods of potash. According to information supplied by the manufacturers twenty-four factories were in operation in 1908, and some of them produced from several thousands up to 200,000 poods of potash. The total production of these factories was from 700,000 to 900,000 poods, representing a value of 22,000,000 rubles. The stems of the sunflower are generally burnt by the farmers themselves. But certain manufacturers also burn the plant buying the stems of 10,000 to 15,000 deciatines, for which they pay 3 to 4 rubles per deciatine. A deciatine of sunflower yields in good ground 200 to 300 poods of stems and in bad ground 100 poods only, from which 3 to 5 per cent of ashes may be extracted, and 3 to 4 poods of ashes give one pound of potash. The percentage of carbonate of potash is 20 to 35 per cent. The appearance of the ash

is improved by a few turns of the wrist, by throwing the salt in the fire for instance, which causes the ash to fuse and gives it a vitreous appearance.

When the sunflower harvest is finished the stems are burnt. The purchase of ashes is finished in September, while the manufacture of potash lasts five to six months. The price of the ashes up to now have been 35 copecks, but owing to competition it has risen to 40 and 60 copecks per pood. The manufacture of potash is conducted in a very primitive fashion; it consists in lixiviating the ashes, methodically concentrating the lye, and in calcining the product. The product is packed in casks of 30 to 40 poods. The analysis of potash from Kuban gave, water, 1.74 per cent; carbonate of potash, 89 per cent; carbonate of soda, 5.0 per cent; sulphate of potash, 2.01; potassium chloride, 6.51 per cent; insoluble by difference, 0.74 per cent; the usual potassium carbonate content is 90 to 91. It is dealt with on a basis of 90 per cent with 2 per cent margin at least. Three-fourths of the potash is exported to Hamburg, London and New York City.

Upon the same principle as that dealt with and described in the manufacture of potash from the sunflower, potash could be manufactured from the seaweed known as kelp. For a long time it has been used and known in the crude state as an excellent dressing for land. Experi-

ments that have been made along the line as described for the sunflower plant, show that from 50 tons of kelp weed, five tons of 20 per cent potash content have been realized. If this process was practiced in the United States under the present stringency of potash shipments from Europe due to the embargo laid on potash on account of the European War, it might have an effect in relieving the farming conditions in this country as they exist at present due to the high price of fertilizers. No experiments that have come under the observation of the writer give any data of the expense of recovering the kelp weed from the sea. It may be that future data will be forthcoming that will make this an industry in the United States of a permanent character.

CHAPTER XIII

ON THE EXAMINATION OF COMMERCIAL FERTILIZERS AND MATERIALS

THE methods here given necessarily include the examination of material used in the manufacture of fertilizers.

Moisture.—Inasmuch as the percentage of moisture in a fertilizer may vary considerably under the conditions to which it is exposed, a determination of moisture is always imperative, in order that the results on other constituents as determined by different analysts, say those of the buyer and the seller, may be fairly compared.

Some analysts invariably heat to a certain temperature (100° to 110° C.) until a constant weight is obtained; others heat for a certain time, 2, 3, or 5 hours, and call the loss moisture. The plan prescribed by the Association of Official Agricultural Chemists is probably most uniformly followed. That is as follows:

For alkaline salts, heat 1 to 5 gms. at 130° to constant weight.

For other material, heat 2 gms. (or 5 gms. if the sample be coarse) for five hours at 100° . The loss in either case is taken as representing moisture.

Phosphoric Acid.—The phraseology regarding the phosphoric acid in fertilizers is often confusing. As may have been inferred, three forms of phosphoric acid are recognized in fertilizers, viz.:

1.—That readily soluble in water, consisting presumably of calcium “superphosphate” ($\text{CaH}_4(\text{PO}_4)_2$).

2.—That not readily soluble in water, but soluble in certain organic solutions, presumably consisting of $\text{CaH}(\text{PO}_4)$ or acid ferric and aluminic phosphates.

3.—That insoluble both in water and in the solvents for No. 2, remaining presumably in the condition in which it originally existed in the phosphate rock.

Notwithstanding the fact of there being numerous possible combinations between phosphoric acid and lime in a fertilizer, it is often required that a report shall show the amount of “bone-phosphate,” to which any given percentage of phosphoric acid is equivalent. The percentage of phosphoric acid multiplied by the factor 2.1831 will give the desired figure.

No. 1 is called “soluble phosphoric acid” or “water-soluble phosphoric acid.”

No. 2 has been called “reverted, inverted, reduced,” etc., phosphoric acid, or, because it is usually determined by washing it out with a solution of ammonium citrate, it has been called “citrate soluble.”

The sum of Nos. 1 and 2 is usually meant

when the term "available" phosphoric acid is employed. English analysts usually apply the term "available" as a synonym for "water soluble," and, on the other hand, the term "soluble" is also sometimes used when the sum of No. 1 and No. 2 is meant.

No. 3 is usually called "insoluble," but to express it more exactly it has also been called "citrate insoluble."

Much of this confusion of terms has arisen from the diversity of opinion as to the utility of the different forms in which the phosphoric acid may be combined.

The sum of Nos. 1, 2, and 3 is called "total phosphoric acid."

Total Phosphoric Acid.—The phosphoric acid is usually separated as the molybdate compound, which is dissolved in ammonia, and precipitated for weighing by magnesium mixture.

As the organic matter of the fertilizer would interfere with the complete separation of the phospho-molybdate, it must be destroyed (usually by ignition, with or without the addition of some nitrate). Hydrochloric acid is the best solvent for ignited phosphates, but the molybdate precipitation is best made in a nitric acid solution, so that, although after ignition hydrochloric acid must be used to effect solution, nitric acid and nitrates should largely predominate when the molybdate separation is effected.

Weigh out 2 gms. of the sample in a platinum

dish, wet down with 5 cc. of magnesium nitrate solution (600 gms. per litre), dry, and ignite. Ignition without addition of nitrate seldom induces error, but is usually slower. After cooling, treat with 5 to 10 cc. of hydrochloric acid, heat, then transfer to a beaker; add about 30 cc. of nitric acid, boil and filter. When the fertilizer contains much iron and alumina more hydrochloric acid should be used. If made up with phosphoric slags, gelatinous silica will appear, which requires evaporation to dryness, and taking up with hydrochloric acid.

A method recommended for fertilizers containing very large quantities of organic matter, consists in boiling with 20 to 30 cc. of concentrated sulphuric acid in a Kjeldahl flask, adding crystals of sodium or potassium nitrate from time to time until the organic matter is destroyed, diluting and filtering. The presence of much sulphuric or hydrochloric acid retards the separation of the molybdate precipitate, and is best avoided. Hydrochloric acid can be removed by evaporating low with excess of nitric acid; sulphuric acid, however, cannot.

In any case, dilute the clear solution to 200 cc., mix well, and take 50 cc. for the analysis (representing 0.4 gm.) With phosphate rock, half this amount will suffice.

Add ammonia until it is just alkaline, then acidify decidedly by addition of 5 cc. of nitric acid; add 10 to 15 gms. of ammonium nitrate

crystals, warm to 80 or 90° C. and add molybdate solution in the proportion of 50 cc. for every 0.1 gm. of phosphoric acid assumed to be present. For ordinary fertilizers which contain less than 20 per cent phosphoric acid, 50 cc. will be ample. Let stand warm, with frequent stirring, until the precipitate settles readily when disturbed; wash by decantation with cold dilute solution of ammonium nitrate acidified with nitric acid, allowing as little as possible of the precipitate to get on the filter. Dissolve the precipitate in ammonia, and precipitate by magnesia mixture, adding it slowly to the clear solution, which is vigorously stirred. Let stand cold for 30 minutes.

Filter upon an ashless filter, wash with water containing one-eighth its volume of ammonium hydroxide, dry, ignite at first with gentle heat, finally at red heat, in a porcelain crucible to constant weight, and weigh as magnesium pyrophosphate.

After ignition this precipitate should be white or light gray in color.

Water-soluble Phosphoric Acid. — Place 2 gms. of the well-ground and mixed sample in a 9-cm. filter and wash with successive portions of water, say 15 to 20 cc. at a time, allowing each lot to run off before the next is added, until the washings measure 250 cc. If the washings contain but little organic matter, one-fifth of the filtrate may be used for the molybdate pre-

cipitation in the manner above indicated, thus determining the water-soluble phosphoric acid directly, or it may be determined indirectly by igniting the filter and contents and determining the phosphoric acid insoluble in water by the method prescribed for "total." In that case use the whole solution from the residue for the determination. The "water soluble" will then be found by difference.

Citrate Soluble Phosphoric Acid.—Take 2 gms., wash out the "water soluble" as before, and then rinse the residue into a 200 cc. flask by use of 100 cc. of absolutely neutral ammonium citrate solution of sp.gr. 1.09. Cork the flask, immerse it in water at 65° and keep it at that temperature for exactly 30 minutes; then filter rapidly, and wash with water of about the same temperature. The "reduced" phosphoric acid is by this means removed. It will, however, be more convenient to determine it indirectly by igniting the filter-paper and contents, and carrying through the determination on the portion undissolved, which really constitutes the "insoluble phosphoric acid."

Ammonium tartrate and also ammonium oxalate, have been used in place of the ammonium citrate, but the results with those salts have been found irregular and unsatisfactory, and their use has been practically abolished. Especial care is necessary to have the citrate solution absolutely neutral—a result not attained by dis-

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solving the ammonium citrate obtained from dealers in water.

Nitrogen.—The absolute method for nitrogen consists in mixing the sample of fertilizer with copper oxide, and then heating to redness in a tube. The carbon and hydrogen take oxygen from the copper oxide becoming carbon dioxide and water, while the nitrogen is set free in the gaseous form. Copper oxide is introduced on both sides of the mixture or sample of fertilizer with the oxide in order to thoroughly burn up any volatile portions coming from the sample. In order to destroy any nitrogen oxides which may be present or be found during the combustion, metallic copper, preferably in the form of a roll of wire gauze, is interposed in the path of the gases to the azotometer, the function of which is to abstract the oxygen from the nitrogen oxides under the conditions produced.

It has been often found that the copper gauze does more than is intended, and abstracts some oxygen from the carbon dioxide as well, giving small amounts of carbon monoxide; so to remedy this a third layer of copper oxide is interposed, which will reoxidize it to carbon dioxide.

To remove the air from the tube at the beginning of the operation, the extreme end of the tube is charged with coarsely crushed carbonate, which on heating evolves carbon dioxide, and sweeps the air from the tube before the combus-

tion is actually begun. The magnesium carbonate is again heated at the close of the operation to drive the nitrogen remaining in the tube into the azotometer.

The azotometer is a graduated tube, with stop-cock above and two side tubes below, at different heights. The lower part of the azotometer as well as the lower side tube is filled with mercury. The upper side tube and the remainder of the azotometer is filled (when ready for use) with a strong solution of caustic potash (to absorb carbon dioxide). The upper side tube is connected with a stop-cock bulb containing the caustic alkali. The bulb is supported in such a way that it can be raised and lowered at will.

The copper oxide should be ignited and cooled before using. The portion which is to be mixed with the substance must be ground in a mortar until it is reduced to a fine sand.

Select a tube of good hard glass which is sealed at one end of a length of about 24 to 27 in. Charge as follows:

Magnesium carbonate, crushed to pieces four or five times the size of a pin's head, $1\frac{1}{2}$ to 2 in.

Coarse granular copper oxide, $1\frac{1}{2}$ to 2 in.

Fine copper oxide mixed with the substance, 4 in. 0.5 to 2 gms. of the fertilizer substance are weighed out in a watch-glass, then mixed with copper oxide, and poured into the tube by the aid of a small paper scoop or funnel. A

little more of the fine copper oxide is then used to rinse off the watch-glass, the whole amount being just about sufficient to fill the tube loosely without shaking down to the depth of about 4 in.

Coarse granular copper oxide, about 8 in.

Metallic copper, preferably in the form of a closely rolled coil of fine wire gauze, 3 in.

Coarse granular copper oxide about 2 in.

Asbestos plug.

Lay the tube so charged in the trough of a combustion furnace and fit tightly into the open end a rubber stopper carrying a glass tube connected by means of a rubber tube with another tube dipping into the mercury in the azotometer.

The end carrying the rubber stopper should project from the furnace far enough to avoid charring the rubber.

Then heat up the magnesium carbonate, starting cautiously at first so as not to break the tube. The air in the tube is thus driven in to the azotometer. When the bubbles of gas rising through the mercury are completely absorbed by the caustic alkali in the upper part of the azotometer, heat up the copper oxide at the other end of the tube, using the same caution as before, carrying the heat slowly back until the metallic copper as well as a couple of inches of the copper oxide on each side of it is at a full red heat. Lower the heat on the magnesium carbonate, pinch the rubber connection between the com-

bustion tube and the azotometer for a moment, open the upper stop-cock of the azotometer, and by raising the bulb force the gas out of the azotometer. Close the azometer stop-cock and release the connection. Then carry the heat slowly back to the mixture of the substance or fertilizer with the copper oxide, getting all of the tube except the magnesium carbonate end finally up to full red heat. The progress of the combustion may be judged by the rapidity with which the bubbles of gas pass through the mercury. It should not be faster than about two bubbles per second.

When they cease, heat up the magnesium carbonate again, keeping up the heat until the gas driven from the tube is all absorbed by the caustic alkali. Then disconnect the azotometer, and cool down the tube. Allow the azotometer to stand for some time to cool completely, and hang it near a thermometer. Bring the bulb close to the azotometer, and raise or lower it until the level of the solution in both is the same. Then read the volume of the gas and the temperature, and calculate the weight of the nitrogen.

When not in use the azotometer should be washed free from caustic alkali, especially as to the stop-cock, which should always be taken out, wiped off, and freshly lubricated with a little vaseline.

Potassium.—Weigh out 10 gms. of fertilizer material. Dissolve in a porcelain evaporating

dish with as little water as convenient, and let boil for 30 minutes. Then render alkaline with ammonia, and add ammonium oxalate in quantity sufficient to precipitate all the lime, cool, and make up to 500 cc. and mix well. Filter and take of the filtrate lots of 25 or 50 cc. according to requirements. Evaporate these down in platinum dishes after acidifying with sulphuric acid, finally igniting the residue until white. Dissolve in a little water, which should give a clear solution; acidify with a drop or two of hydrochloric acid; add 5 cc. of platinum chloride, evaporate to a pasty condition; add 30 cc. or more of strong alcohol (80 per cent or over), allow to stand cold for some time, and then decant on weighed filter and add fresh alcohol, and repeat two or three times, and then transfer to filter and wash with ether; dry, cool in desiccator, and weigh. From total weight deduct weight of filter-paper, or a Gooch crucible with asbestos filter may be used. Precipitate is K_2PtCl_6 . In place of alcohol a mixture of alcohol and ether is preferable in proportions of 2 to 1.

Regarding the examination of phosphatic materials to be used in the manufacture of fertilizers, a few suggestions may be desirable.

Spent bone-black and other materials containing carbon or carbonaceous material as well as phosphate rock, may be ignited to burn off the organic substances, then dissolved in hydrochloric acid, and in general treated essentially

as recommended for the determination of total phosphoric acid.

With phosphatic slags the first hydrochloric acid solution should be evaporated to dryness in order to remove the silica (which would otherwise appear in gelatinous form). Before proceeding with phosphate rock, the proportion of iron and alumina oxides is of much importance on account of their tendency to afford the so-called "reduced phosphate" in the finished product. A good method consists in dissolving the sample in aqua regia, adding sulphuric acid, and then a large excess of alcohol, which precipitates the calcium sulphate. In the clear alcoholic solution the iron and alumina, as phosphates, may be determined.

Another plan affording good results when carefully conducted would be to dissolve 2.5 gms. of the material in 10 cc. of hydrochloric acid and 1 or 2 cc. of nitric acid. Then add 10 cc. of concentrated sulphuric acid, mix in well, and add strong alcohol, 90 per cent or over, in sufficient quantity to bring the bulk of the solution, when well mixed and cold, up to 250 cc. Shake well, and allow to settle for 30 to 60 minutes. Then filter off rapidly 200 cc. (representing 2 gms.), neutralize very exactly with ammonia, boil out the alcohol, avoiding evaporation to dryness, and then render alkaline with a little ammonia, boil and filter. The precipitate, consisting of iron and alumina phosphate, is

ignited and weighed by some, and half its weight taken as that of the iron alumina oxide, which roughly speaking is true. It is, however, more exact and satisfactory to dissolve the moist hydrates in nitric acid, neutralize closely, precipitate out phosphoric acid with a sufficient but not too large excess of ammonium molybdate, letting it stand warm for some hours, and in the filtrate precipitate with ammonia, boiling out the excess to render the alumina insoluble. Filter, and then treat the precipitate with about 10 cc. of strong ammonia to dissolve out the molybdic acid, wash again, and dry, ignite, and weigh the mixed oxides.

If desired, the precipitate may be brought into solution, and the iron reduced and titrated in the usual manner, the alumina being obtained by difference.



CHAPTER XIV

ON THE EXAMINATION OF SOILS

SURFACE accumulations of decaying leaves should be removed and a slice of uniform thickness from the surface to the desired depth should be secured. To eliminate the effects of accidental variations in the soil, select specimens from five or six places in the field and remove several pounds of the soil to the depth of six inches, or to the change between the surface soil and the subsoil, in case such change occurs between the depth of six and twelve inches. In no case is the sample to be secured to a greater depth than twelve inches. If the surface soil extend to a greater depth, a separate sample below the depth of 12 inches is to be obtained. If the surface soil extend to a depth of less than 6 inches, and the difference between it and the subsoil is usually great, a separate sample of the surface soil should be secured, besides the one to the depth of six inches.

The depth to which the sample of subsoil should extend will depend on circumstances. It is always necessary to know what constitutes the foundation of a soil, to the depth of three feet at least, since the question of drainage,

resistance to drought, etc., will depend essentially upon the nature of the substratum. But in ordinary cases 10 or 12 in. of subsoil will be sufficient for the purposes of examination in the laboratory. The specimen should be obtained in other respects precisely like that of the surface soil, while that of the material underlying this subsoil may be sampled with less exactness, perhaps at some ditch or other easily accessible point, and should not be broken up, but left, as nearly as possible, in its original state. Mix each of these soils intimately, remove any stones, shake out all roots and foreign matter, expose in thin layers in a warm room till thoroughly air-dry, or dry in an air-bath at a temperature of 40° C.

The soil is rapidly dried to arrest nitrification. It is not heated above 40° lest there be a dissipation of ammonium compounds, or a change in the solubility of the soil. The normal limit to which the soil may be heated in place by the sun's rays should not be exceeded in preparing a soil for an agricultural chemical analysis.

Five hundred gms. or more of the air-dried soil, which may be either the original soil or that which has been passed through a sieve of coarser mesh, are sifted through a sieve with circular openings one-half millimeter in diameter, rubbing, if necessary, with a rubber pestle in a mortar until the fine earth has been separated as completely as possible from the particles that are too coarse to pass the sieve. A three-

millimeter sieve should be used when the determinations are made on 100 gms. or more of soil. The fine earth is thoroughly mixed and preserved in a tightly stoppered bottle, from which the portions for analysis are weighed.

The coarse part is weighed and examined microscopically or with Thoulet's solution.

It may sometimes be necessary to wash the soil through the one-half millimeter sieve with water; but this is to be avoided whenever possible.

Determination of Moisture.—Heat from 2 to 5 gms. of the air-dried soil in a flat-bottom, tared platinum dish for five hours in a water oven kept briskly boiling; cover the dish, cool in a desiccator, and weigh. Repeat the heating, cooling, and weighing at intervals of two hours till nearly constant weight is found, and estimate the moisture by the loss of weight. Weigh rapidly, to avoid absorption of moisture from the air.

Determination of Volatile Matter.—Heat the dish and dry soil from the above determination to full redness, until all organic matter is burned away. If the soil contains appreciable quantities of carbonates, the contents of the dish, after cooling, are moistened with a few drops of a saturated solution of ammonium carbonate, dried and heated to dull redness to expel salts of ammonia, cooled in a desiccator, and weighed. The loss in weight represents the organic matter, water of combination, salts of ammonium.

Determination of Acid-soluble Materials.—In the

following scheme for soil analysis it is intended to use the air-dried soil from the sample bottle for each separate investigation. The determination of moisture, made once for all on a separate portion of air-dried soil, will afford the datum for calculating the results of analysis upon the soil dried at the temperature of boiling water. It is not desirable to ignite the soil before analysis, or to heat it so as to change its chemical properties.

The acid digestion is to be performed in a flask so arranged that evaporation of acid shall be reduced to a minimum, but under atmospheric pressure and at the temperature of boiling water. The digestion is easily accomplished in a flat-bottom conical flask of hard glass, carrying a stopper and hard-glass condensing tube at least 18 in. long. Where sulphuric acid is to be determined a rubber stopper cannot be used. A flask with ground-glass stopper, carrying a condensing tube, is useful in such cases.

The flask must be immersed in the water-bath up to the neck, or at least to the level of the acid, and the water must be kept boiling continuously during the digestion.

In the following scheme 10 gms. of soil are used, this being a convenient quantity of most soils, in which the insoluble matter is about 80 per cent. If desired, a larger quantity of such soil may be used, with a proportionately larger quantity of acid, and making up the soil

solution to a proportionately larger volume. In very sandy soils, where the proportion of insoluble matter is 90 per cent or more, 20 gms. of soil are to be digested with 100 cubic centimeters of acid and the solution made up to 500 cc.; or a larger quantity may be used, preserving the same proportions. It is very important that the analyst assure himself of the purity of all the reagents to be used in the analysis of soils before beginning the work.

In a flask of 200 cc. capacity place 10 gms. of air-dried soil and 100 cc. of hydrochloric acid. Close flask with cork, carrying a glass tube about 2 ft. in length to act as reflux condenser. Place flask in water-bath and keep at boiling temperature for ten hours with occasional shaking. Transfer contents of flask to a beaker, and bring residue on to filter and wash with distilled water; dry residue and weigh as insoluble material. Make solutions and washings up to 500 cc. with distilled water.

Iron and Alumina.—100 cc. of above solution are made slightly alkaline with ammonia, then boiled to expel excess of ammonia, filtered, and well washed with hot distilled water. The precipitate is iron, alumina and phosphates. After drying, igniting in tared crucible, and weighing the desiccated product, the iron and alumina may be separated as follows: Bring residue of iron and alumina into a beaker, add 15 cc. of dilute sulphuric acid (1 of acid and 4 of

water), heat on water-bath with beaker covered until in solution, then determine iron with potassium permanganate by volumetric method, and from these results and total, iron and aluminium phosphate estimate the amount of iron and alumina.

Manganese.—The filtrate above is concentrated to about 100 cc., ammonia added to alkalinity, bromine water added and the solution heated to boiling. Allow the solution to cool and add more bromine water and ammonia, and heat as before to precipitate all the manganese; acidify with acetic acid, and filter while still boiling, wash with hot water and ignite as manganous manganic oxide, Mn_3O_4 .

Calcium.—Evaporate above filtrate to about 50 cc., add ammonia to slight alkalinity, and to the hot solution add ammonium oxalate and allow to stand twelve hours, filter, and wash with hot water containing a little ammonia; dry, and transfer precipitate to tared platinum crucible; burn filter-paper, add ash to the crucible, and ignite, at first slowly and finally with full blast; cool, and weight as calcium oxide.

Magnesia.—If necessary concentrate the filtrate above, make alkaline with ammonia, add Na_2HPO_4 until no further precipitate occurs, stir carefully without touching sides of beaker, and allow to stand until solution above precipitate is perfectly clear. Filter and wash out beaker with portions of the filtrate, and then

wash with diluted ammonia water (1 part ammonia to 8 parts water) until filtrate gives no coloration with nitric acid and silver nitrate. Dry thoroughly, remove precipitate to tared porcelain crucible, burn filter-paper and add the ash to the crucible and its contents, and ignite, at first slowly, then to intense heat; cool, and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$.

Alkalies.—To the last filtrate add ammonia, boil to expel excess of ammonia, filter and wash. Evaporate the filtrate to dryness, heat below redness to expel ammonia salts, add 30 cc. of water, then a few drops of barium hydroxide solution, and heat to boiling. Filter and wash with hot water. To the filtrate add ammonia hydroxide and ammonium carbonate, filter, and wash with hot water. Evaporate to dryness and determine potassium by adding platinic chloride to slight excess, and evaporate almost to dryness on water-bath; then add 40 cc. of 80 per cent alcohol, and allow to stand for one hour; then decant on weighed filter and add fresh alcohol, and repeat two or three times, and then transfer to filter and wash with ether; dry, cool in desiccator, and weigh. From total weight deduct weight of filter-paper, or a Gooch crucible with asbestos filter may be used. Precipitate is potassium platinic chloride. In place of alcohol a mixture of alcohol and ether is preferable in proportion of 2 and 1.

Sodium.—The mixed alkalies are weighed as

chlorides, the solution having been evaporated to dryness and the ammonium salts expelled by heating to dull redness. Dissolve the precipitate with 10 cc. of water and add platinic chloride as in potash determination, precipitating potash and sodium. After evaporating dissolve the sodium platinic chloride out with alcohol, leaving potassium platinic chloride to be dried and weighed for the potash determination. The sodium can be determined by difference of the total weight of alkalies.

Carbon Dioxide.—In five grams of the air-dried soil determine carbon dioxide by mixing with about four times its weight of powdered borax, and fuse. Weigh and the loss in weight can be taken as carbon dioxide.

Nitrogen.—Of the air-dried soil weigh out three grams, place in a digestion flask, add 30 cc. of concentrated sulphuric acid (sp.gr. 1.84) containing one gram of salicylic acid, and thoroughly mix by shaking. Heat over a low flame until no further frothing, and then boil briskly for five or ten minutes; now add about 0.7 gram of mercuric oxide, and continue the boiling until the solution is colorless; then complete the oxidation by adding slowly fine pulverized potassium permanganate to the hot solution, until after shaking the solution is green or purple in color. Transfer the contents of the cool flask to a distilling flask, using about 100 cc. of water, and add a few pieces of granulated zinc to prevent bumping;

now add 30 cc. of potassium sulphide solution (40 grams in 1000 cc. water), and after shaking add 80 cc. of a saturated caustic soda solution or enough to make it alkaline. Connect at once with the condenser, and distill over about 125 cc., receiving into a measured quantity of standard acid, and then titrate with standard alkali, using cochineal as indicator. One cc. of the decinormal sulphuric acid is equal to .0014 gram of nitrogen.

In the absence of nitrates the salicylic acid may be omitted from the sulphuric acid; otherwise the nitrogen determination is made the same way as above, with varying amount of substances to be analyzed, according to its nitrogen content.

Phosphoric Acid.—Ten grams of the sifter soil, dried at 100° C., are charred if organic matter be present. The charred mass is moistened with water and afterwards with nitric acid, until the carbonates are decomposed. The mass is digested with ten cubic centimeters of nitric acid for two hours at about 100° C. with frequent stirrings and the addition of fresh acid, from time to time, to replace that which has been evaporated. After filtering and washing with hot water the filtrate is evaporated to a volume of 50 cc. and treated with five cubic centimeters of concentrated nitric acid and half a gram of crystals of chromic acid. After covering the dish with a funnel to return condensed vapors its contents are heated to the boiling

point for half an hour to complete the destruction of organic matter. At the end of this time five grams of ammonium nitrate are added to facilitate the precipitation of the phosphoric acid, and 50 cc. of molybdate solution, and the mixture kept at a temperature of about 100° C. for an hour. The precipitate obtained is washed twice by decantation with water containing one-fifth of its volume of ammonium molybdate solution. It is dissolved in 30 cc. of ammonia diluted with an equal bulk of warm water. The solution and washings should measure 80 cc. and the ammonia therein is neutralized with nitric acid, keeping the temperature below 40° C. When the yellow precipitate formed ceases to redissolve on stirring, that is, when the ammonia has been neutralized, a mixture of 3 cc. of pure nitric acid and 5 cc. of water is added, together with the same quantity of molybdate solution. After standing for two hours at 40° C. the precipitate is brought upon a filter, washed first with water containing 1 per cent of nitric acid, and finally with a little pure water, and dried at 100° C. and weighed. The weight of the precipitate multiplied by the factor 0.0373 gives the quantity of phosphoric acid. The object of the second precipitation is to relieve the process of the necessity of rendering the silica insoluble, as the presence of silica in the solution as above treated does not interfere with the complete precipitation of the phosphate.

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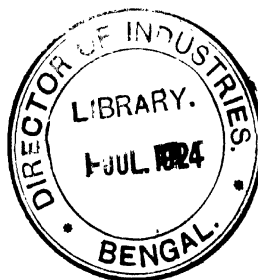
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